PREFACE

This document is Volume 11 of a series of reports entitled "Geological Evolution and Analysis of Confirmed or Suspected Gas Hydrate Localities." Volume 11 provides an analysis of the Black Sea region. The report presents a geological description of the Black Sea region, including regional and local structural settings, geomorphology, geological history, stratigraphy, and physical properties. Included also is a discussion of bottom simulating acoustic reflectors, sediment acoustic properties, distribution of hydrates within the sediments, and the relation of hydrate distribution to other features such as salt diapirism. The formation and stabilization of gas hydrates in sediments are discussed in terms of phase relations, nucleation, and crystallization constraints, gas solubility, pore fluid chemistry, inorganic diagenesis, and sediment organic content. A depositional analysis of the area is discussed in order to better understand the thermal evolution of the locality and to assess the potential for thermogenic hydrocarbon generation.

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EXECUTIVE SUMMARY

This report presents one of the 24 locations designated by the U.S. Department of Energy (DOE) - Morgantown Energy Technological Center (METC) for study of gas hydrate formation and stability in geological environments.

The Black Sea is located in extreme southeastern Europe between two prominent Alpien mountain ranges, Crimea and the Caucasus on the north and the Pontic Mountains on the south. The total area of this world's largest enclosed marine basin is approximately 432,000 km^2.

The region of the Black Sea was listed by Kvenvolden and Barnard among the worldwide locations with confirmed occurrence of gas hydrates. This listing was principally based on the information published by Yefremova and Zhizhchenko (1972). According to these authors, gas hydrates were found at the Black Sea station 116, at 6.4 to 8.1 m subbottom depth. The water depth at the station was reported to be 1,950 m. Unfortunately, neither the precise location of the site nor more geological or geochemical data were published. Makogon (1974) also wrote about frost-like hydrate crystals observed on broken surfaces of cores from the Black Sea.

In the mid 1970s, a variety of investigations were launched in the Black Sea during cruises of Atlantis II (1974) and Glomar Challenger (1975). Although none of these investigations was specifically designed for gas hydrate research, they provided some important data related to varying conditions of geological environment in the basin. Knowledge of these conditions is crucial for the delineation of the areas favorable for gas hydrate formation, as well as the areas where gas hydrate occurrence cannot be anticipated. Analysis of the Black Sea basin strongly suggests that, in the areas characterized by temperatures and pressures within the gas hydrate stability range, their distribution is most likely controlled by methane concentrations. The calculations made have demonstrated that favorable temperature-pressure conditions in the Black Sea start at approximately 900 m sea depth. The lower boundary of the gas hydrate stability zone may extend from 0 to 323 m subbottom depth at water column 900 to 2,000 m respectively.

All geological expeditions to the Black Sea have revealed substantial amounts of hydrocarbon gases escaping from recovered cores. Geochemical analyses of these gases have invariably shown their biogenic provenance. Indeed, the Black Sea has been known for extensive biogenic methanogenesis. The sea water stratification effectively prevents water exchange between its upper and lower strata. The lack of these water mixing processes establishes a thick chemical reducing zone which enables the sinking organic matter to be preserved to a significant degree. The preserved organic matter constitutes a prime raw material indispensible in the processes of microbial methanogenesis. In the vertical profile through the water and sediment column of the Black Sea, the typical succession of bacterial environments described by Claypool and Kaplan (1974) is easily discernible. The reducing conditions usually start to occur at 150 to 200 m water depth. It has been estimated that the main source of the organic matter supplied to the Black Sea is unicellular algae (90 to 95% organic matter) produced in the process of photosynthesis. Only 10% of the total organic matter is delivered to the basin in detrital form by rivers. Yet, despite very favorable conditions for biogenic methanogenesis, the pore water in the nearbottom sediments of the western Black Sea was found largely undersaturated. Assuming the accuracy of the measurements of methane content in sediments presented by Ivanov (1984), it can be concluded that the average values are far below those needed for gas hydrate generation and stabilization (Claypool and Kaplan, 1974). Therefore, gas hydrate formation in the Black Sea region is conceivable in those areas of higher concentrations of methane gas, which perhaps coincides with rock formations with increased porosity and permeability. Such areas probably have a patchy character throughout the basin, and their identification must await more factual data in the field of sedimentation and lithology.

With the assumption that the zone favorable for gas hydrates in the Black Sea extends over 1% of the area delineated by the 900 m isobath, the estimated resources of hydrocarbon gas in gas hydrates amounts to 2×10^{10} m^3 (0.7 TCF) per 1 m of the zone's thickness.

INTRODUCTION

The Black Sea region represents one of the few locations worldwide where the presence of gas hydrates was directly confirmed in recovered cores (Yefremova and Zhizhchenko, 1972) at the station 116. Besides this location, Russian authors reported the presence of ice-frostlike crystals of gas hydrates in a number of cores from unspecified parts of the Black Sea.

In this study, the principal factors of gas hydrate formation are considered in the context of geological environment. With regard to the temperature and pressure conditions necessary for gas hydrate stability, over 255,000 km^2 out of the total 432,000 km^2 were found to represent the potential gas hydrate zone. Such territorial extent, however, proved to be further limited by the availability of gases indispensable for gas hydrate formation processes. Generation and distribution of the hydrocarbon gases are perhaps the most important factors controlling the potential gas hydrate zone. Practically all geochemical characteristics of the hydrocarbon gases from the Black Sea sediments showed invariably their biogenic origin. Strong efforts were made to present and explain the maximum of the available data. Some of the Russian data used have not been published in English.

The bottom simulating reflectors (BSRs) commonly used to identify lower boundaries of the gas hydrate zone turned out to be of little help in the Black Sea. This is largely due to the fact that the sediments have stratification predominantly parallel to the sea floor throughout the entire basin.

ACKNOWLEDGEMENTS

The authors of this report wish to express their gratitude to the Department of Energy, Morgantown Energy Technology Center, for the opportunity to participate in the gas hydrate research program. With regard to data collection from the region of the Black Sea, our words of appreciation go to Professor Trotsyuk who provided us with the book <u>Oil and Gas Investigations in the Bulgarian Sector of the Black Sea</u>, which served as a rich source of geological data. Also comments and suggestions made by Kathryn Dominic were invaluable.

PART I

BASIN ANALYSIS

Location

The Black Sea, which occupies an area of approximately 432,000 km^2, represents one of the world's largest enclosed marine basins. This semi-isolated marine basin is located in extreme south-southeastern Europe between two Alpine mountain ranges, the Crimea and Caucasus Mountains to the north, and the Pontic Mountains to the south. The longer axis of the elliptical Black Sea extends in west-east directions between longitudes 27°40'E and 43°40'E, whereas the meridional extent of the sea is from the approximate latitude 41°N to 46°30'N (Figure 1).

Geomorphology

The first detailed study of the geomorphology of the floor of the Black Sea was made by V.P. Goncharov in 1956-1958 at the Soviet Institute of Oceanology (Goncharov, 1958). In 1974, Goncharov's bathymetric chart of the Black Sea was supplemented by another bathymetric map of the same area which was based on additional echo-sounding data collected from the R/V Atlantis II of the Woods Hole Oceanographic Institution in 1969 (Ross et al., 1974). Despite minor differences in depth, which mostly resulted from various acoustic velocities applied, the two charts reflect similar geomorphological features of the Black Sea floor.

Four major geomorphological provinces are easily discernible within the Black Sea: shelf, basin slope, basin apron, and abyssal plain (Figures 1 and 2).

The shelf is generally limited by a 100 m isobath with the exception of some areas off the Crimea peninsula and Sea of Azov where the limits of the shelf coincide with slightly greater depths (approximately 130 m). This province has maximum development west of the Crimea peninsula where its width exceeds 190 km. A relatively narrow shelf area, rarely wider than 20 km, has been found along the southern flanks of the Black Sea basin as well as in the area south of the Crimea peninsula. The intermediate widths of the shelf are found off the Bulgaria coast and south of the Sea of Azov. The average width of the shelf in the latter area is 40 km. Goncharov and Neprochov (1967) suggested the presence of ancient river channels across the shelf west of the Crimea and submarine canyons on the edge of the outer shelf, indenting the shelf landward.

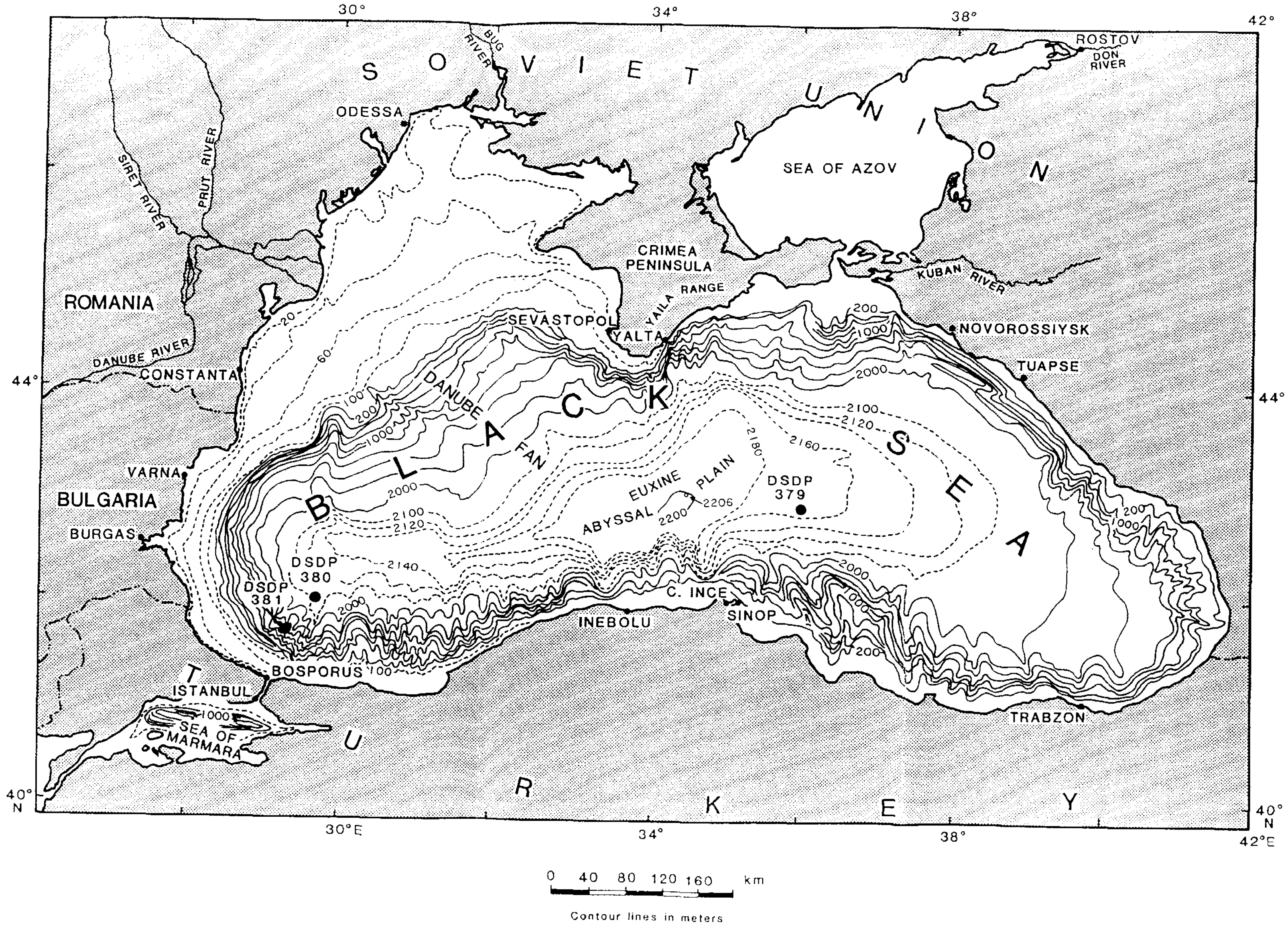
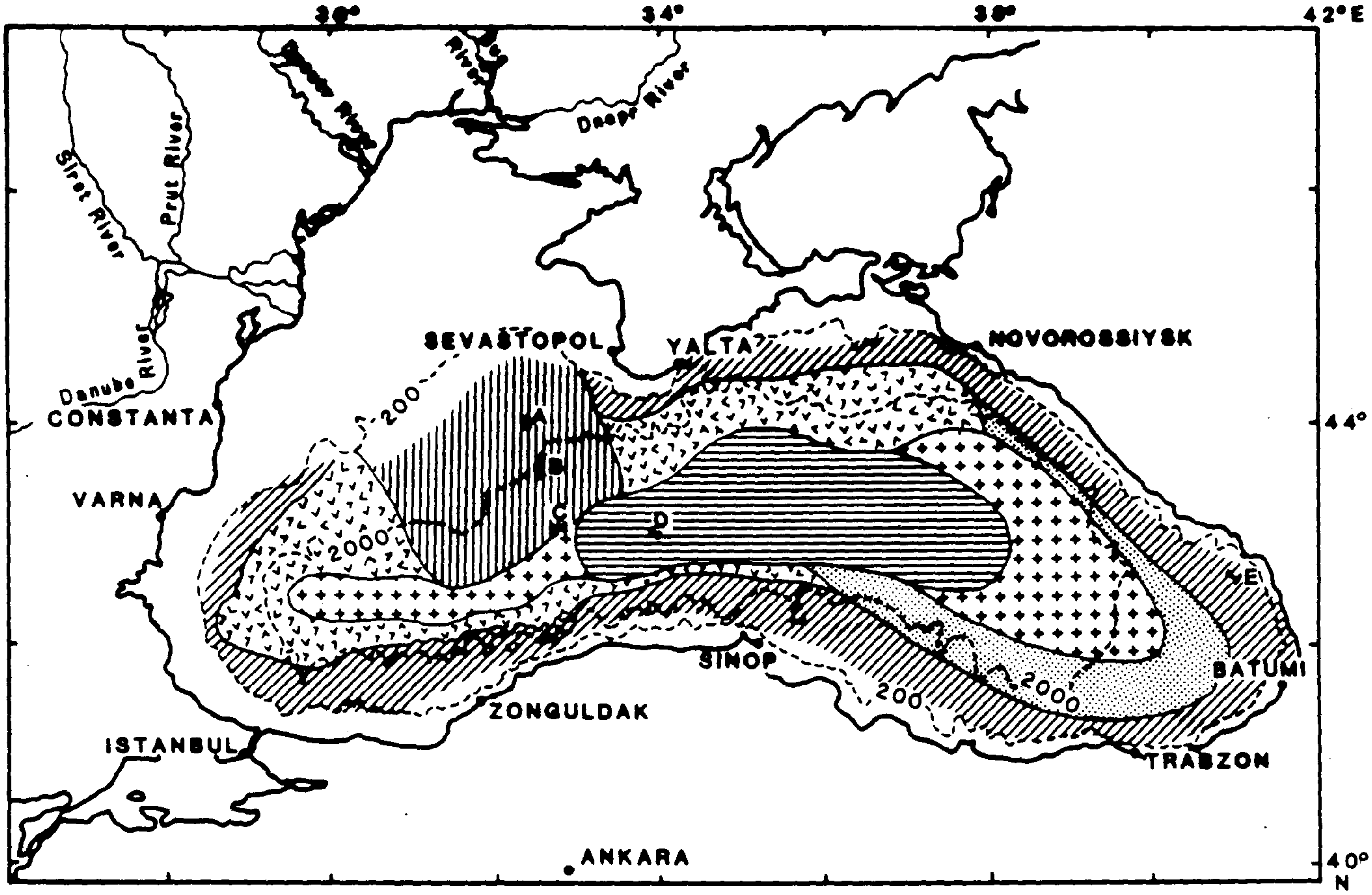


Figure 1. BATHYMETRIC MAP OF THE BLACK SEA

After Degens and Ross, 1974



LEGEND

12 kHz BOTTOM CHARACTERISTICS	RATES OF DEPOSITION DURING THE LAST 3000 YEARS IN cm/10^3 yrs
ROUGH TO UNDULATING BOTTOMS; STRONG ECHO; SUB-BOTTOM ON CREST OF RIDGES	>30
UNDULATING BOTTOM; STRONG ECHO; NO SUB-BOTTOMS	>30
FLAT BOTTOM; STONG ECHO; NO SUB-BOTTOMS	>30
FLAT BOTTOM; STRONG ECHO; SUB-BOTTOM REFLECTORS	10-30
UNDULATING BOTTOM; STRONG ECHO; SUB-BOTTOMS	10-30
UNDULATING BOTTOM; MUSHY ECHO; NO SUB-BOTTOMS	0-10

Figure 2. BLACK SEA BOTTOM SURFACE CHARACTERISTICS BASED ON ECHOGRAMS OBTAINED DURING "ATLANTIS II" CRUISE

After Ross et al., 1974

The basin slope within the Black Sea is represented by two main sea-floor gradients. Typical for continental slopes, a gradient of 1:40 is present along the southern slope of the Black Sea off the Caucasus Mountains and off the Crimea peninsula. These sections of the basin slope appear to be highly dissected by submarine canyons. The submarine canyons often reveal their extension across the basin apron. The extension of the canyons oblique to the slope indicates their structural controls. Also a number of submarine ridges parallel or oblique to the slope revealed off the Caucasus Mountains are thought to be mostly structurally controlled.

The second type of basin slope is represented by smooth slopes with many parallel gradients. This type of slope has been identified in the adjacent area to the broad shelf west of the Crimea and southwest of the Sea of Azov. According to Ross et al. (1974) the latter type of Black Sea basin slope is related to Ukranian shield areas and reflects "either a thick sedimentary blanket or a major structural difference between the platform area and the mountainous regions of the Black Sea".

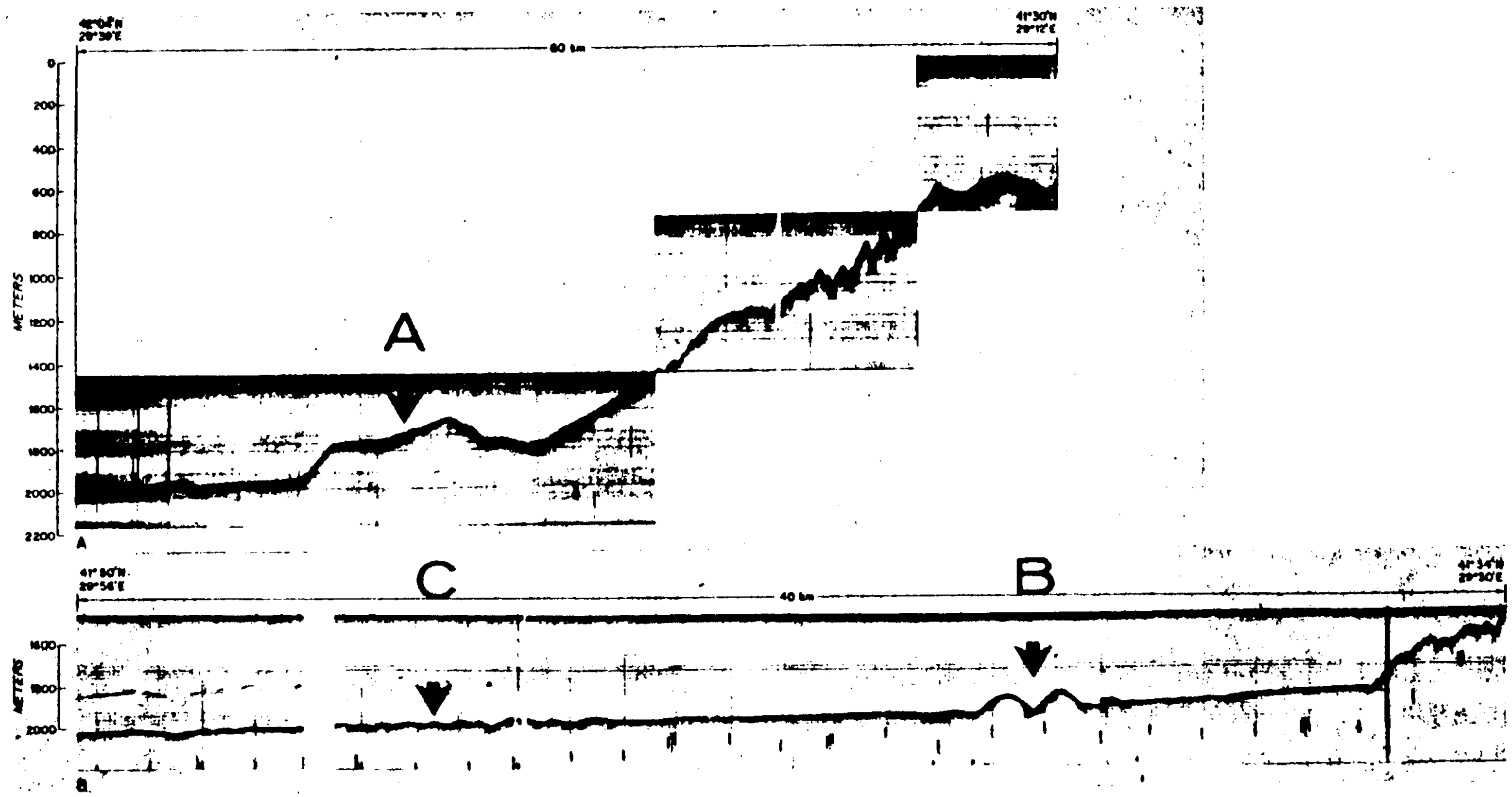
The basin apron occupies the next circular zone toward the axial part of the Black Sea. Adjacent to the basin slope areas, the slope gradients show values typical for a continental rise between 1:40 and 1:1,000. Danube fan (Figure 1) constitutes a distinct depositional feature which divides the central abyssal plain of the Black Sea into two unequal parts. Analyses of the seismic sections indicate that the fan sediments were deposited by the Danube, Dnestr, Bug, and Dnepr Rivers. The studies of Holocene sediments of the rivers showed that an insignificant amount of the fluvial material is presently supplied to the fan; most of the detritus is unloaded in estuarine areas. Therefore, it had been concluded that the Danube fan was deposited in the Pleistocene when the sea level was lower and deltaic conditions prevailed.

On the relatively smooth surface of the basin apron of the Black Sea, quite intriguing positive geomorphological forms, known from the oceanic basins as "lower continental-rise hills" (Ballard, 1966; Emery, 1970), were identified. Ripples about 40 km high at a depth of 1,900 m identified near Bosporus were described by Lacombe (1960). Some similar features from the cruise of the R/V Atlantis II in the Black Sea recorded on echograms are shown on Figure 3.

The large block-like rectangular form marked by A (Figure 3) has been interpreted as a partly buried slump block. Such forms are common on the eastern side of the basin and reach the size of 30 k in width. The presence of these forms may be indicative of the important sediment mass movement in the Black Sea basin.

The euxine abyssal plain occupies the central part of the Black Sea. In this almost flat area, a maximum depth of 2,206 m has been measured in the basin. Ross et al. (1970) suggested that better development of the euxine abyssal plain in its eastern section is probably caused by greater activity of turbidity currents in this area.

The areal percentage of all four provinces within the Black Sea is shown in Table 1.



A, B, C correspond to the sections marked in Figure 2.

Figure 3. ECHOGRAMS FROM THE WESTERN PART OF THE BLACK SEA

After Ross et al., 1974

TABLE 1.

AERIAL EXTENT OF THE BLACK SEA BATHYMETRIC PROVINCES, After Ross et al., 1974

PROVINCE	PERCENTAGE AREA
Shelf	29.9
Basin slope	27.3
Basin apron	30.6
Abyssal plain	12.2

Structural Setting

The Black Sea basin is surrounded to the north, northeast, south and southeast by the Alpine folded systems of Crimea, Caucasus, Asia Minor and southern Balkans (Figure 4). In the northwestern direction, the basin is bordered by the epihercynian platform known as the Ukranian shield. Geological and geophysical studies have shown that part of these major tectonic structures may be identified under nearshore areas of the present basin.

Despite the considerable amount of knowledge accumulated on the Black Sea basin and adjacent regions, there is a lack of consensus as to the age and origin of the Black Sea. The age estimates range from early Precambrian (Malinovskiy, 1967) to early Quaternary (Nalivkin, 1960). Most scientists seem to favor middle and late Mesozoic to Tertiary age (Brinkmann, 1974; Muratov, 1975). Muratov (1975) suggested that geologic history of the Black Sea consists of three distinct periods. During the first period from Mesozoic to Paleogene, a relatively shallow basin was located in the Black Sea area while two deep geosynclinal depressions existed to the north and south of the shallow area. The second period in Oligocene and Miocene was marked by the presence of several deep basins filled with sediments in the central, northern, western and eastern parts of the Black Sea. The present deep basin of the Black Sea evolved during the third period in Pliocene and Pleistocene time.

Gravity, magnetic and seismic reflection data from the Black Sea showed that the recent subsidence of this area coincides with fault systems along the southern, eastern, and northern parts of the basin (Figure 5). At the same time the western margin of the Black Sea remained tectonically relatively quiet. Local patterns of the gravity field seem to confirm the presence of a separate structure for the eastern and western parts of the basin (Ross et al., 1974). A typical large Bouger anomaly was measured over most of the Black Sea, whereas free air gravity anomalies are usually negative. Continuous seismic profiles from the Black Sea show deep-seated faults which are particularly frequent along its southern and eastern sections. Studies performed by Ross et al. (1974) also revealed that, except in the western part of the Black Sea, slumping and downfaulting are fairly common in most of the basin margin. Within the basin apron the seismic horizontal reflectors can be traced for several hundreds of kilometers in low velocity, upper sedimentary

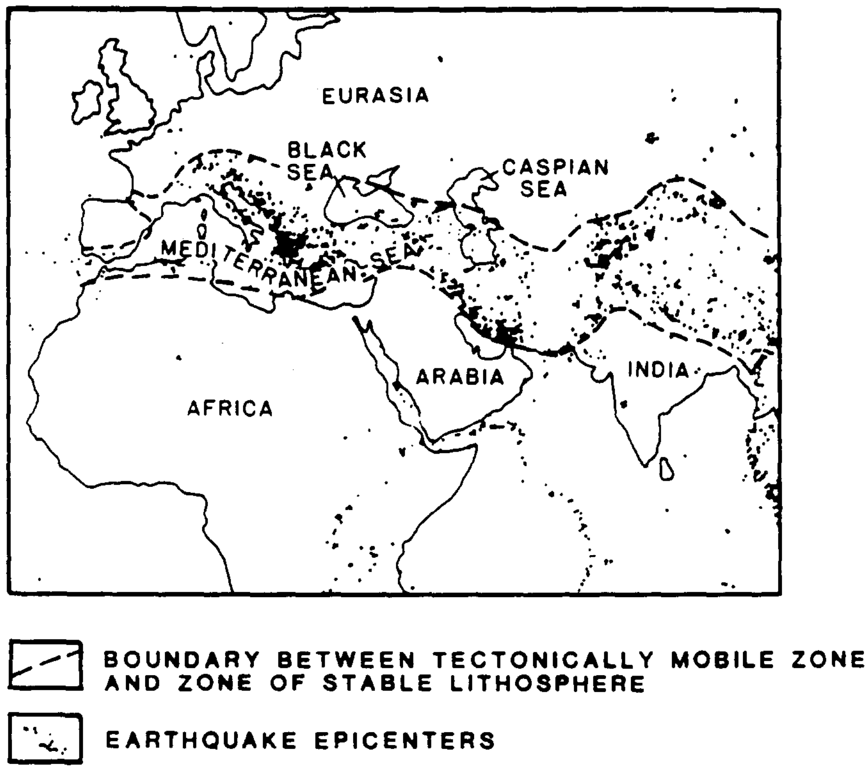


Figure 4. **MAP SHOWING LOCATION OF BLACK SEA AT NORTHERN EDGE OF ALPINE-HIMALAYAN REGION**

After Erickson and Simmons, 1974

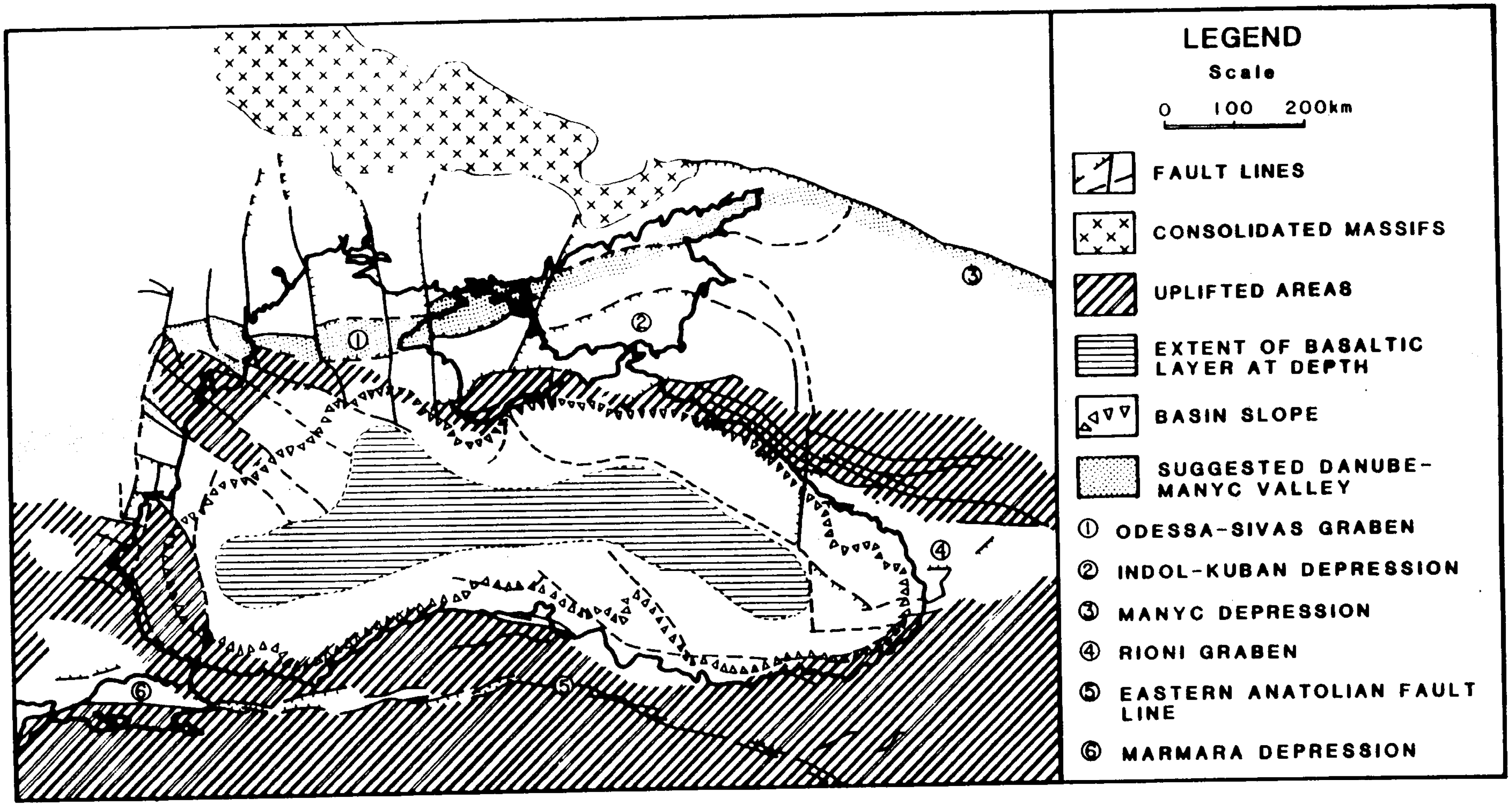


Figure 5. **TECTONIC MAP OF THE BLACK SEA REGION**

Compiled by Degens and Paluska, 1979

units. In some places (e.g. south of the Crimea), the continuous layers are interrupted by small, steep, normal faults. These faults probably constitute the structural zone running across the Black Sea in a northwest-southeast direction. The strata probably folded during the Caucasus orogeny were interpreted in the central part of the sea.

One of the important issues of the tectonic position of the Black Sea is the type and structure of the underlying crust. The accumulated seismic, magnetic, and gravimetric data seem to suggest that the crustal structure of the Black Sea is intermediate between continental and oceanic. Neprochov et al. (1970) noted the similarity of the crustal structures to those found in the Mediterranean and Caspian seas which would testify to the common origin of the crusts. The general alignment of the Caucasus and Pontic mountains with the west-east direction suggests that the Black Sea area underwent compression along the north-south direction. The more recent development of the Black Sea, including its coastal parts, seems to be dominated by subsidence (Belavadze et al., 1966; Tzagareli, 1974).

Analysis of the acoustic velocities in vertical profiles in various parts of the Black Sea led some authors to intriguing conclusions as to the structural features of the basin (Neprochov, 1962; Goncharov et al., 1972; Neprochov et al., 1975; Ross et al., 1974; Letonzey et al., 1975). A deep seismic sounding survey performed by the Soviets revealed that the crust in the central part of the Black Sea consists of two main layers (Figure 6). The upper sedimentary layer, with characteristic seismic velocity of 3-3.5 km/sec, is approximately 8 to 16 km thick. This layer is underlain directly by a 5,000 m to 10,000 m thick layer with acoustic velocities of 6.6 to 7.0 km/sec, typical for basalt. At the same time, velocities of 6 to 6.4 km/sec, indicating the presence of granite, were found in the continental areas surrounding the Black Sea. Neprochov and Ross (1974) pointed out two possibilities for the origin of this "granite free" area: either it constitutes the relict ocean crust or it was formed in place. Existing data do not seem to favor definitively either of these possibilities. The oceanic origin of the crust in the Black Sea area suggested by Milanovskiy (1967) remains in contradiction with its excessive thickness (14,000 m to 18,000 m) compared with known oceanic crusts. Also, the hypotheses which involve transformation of continental crust into an intermediate, more oceanic type of crust do not satisfy the presently known structural features of the crust in the Black Sea. Ross (1974) indicated two conceivable ways of transformation of the continental crust into more oceanic crust. One would be in situ conversion of low-density thick continental crust into a denser and thinner more oceanic crust. The second possibility would result from replacement of the continental crust by upwelling mantle material along cracks or extension fractures. Again, both solutions present serious deficiencies. For example, the extensional origin of the crust can be argued against by the continuity of geologic structures around the Black Sea and magnetic trends paralleling these structures and extending into the basin. Additional difficulties in the interpretation of the above two theories are caused by the presence of a landward thickening ring of a "granitic" layer (Figure 6). The latter argument has been included in hypotheses of the Black Sea basin evolution presented by Erickson and Simmons (1974) and Brinkmann (1974). According to Erickson and Simmons, the Black Sea originated with the convergence of the Eurasian and African plates. At this time the upper parts of the crust would have been removed. When the rate of subduction decreased or ceased, the following temperature in the mantle caused the crust and the lithosphere to sink with increasing sedimentation taking place.

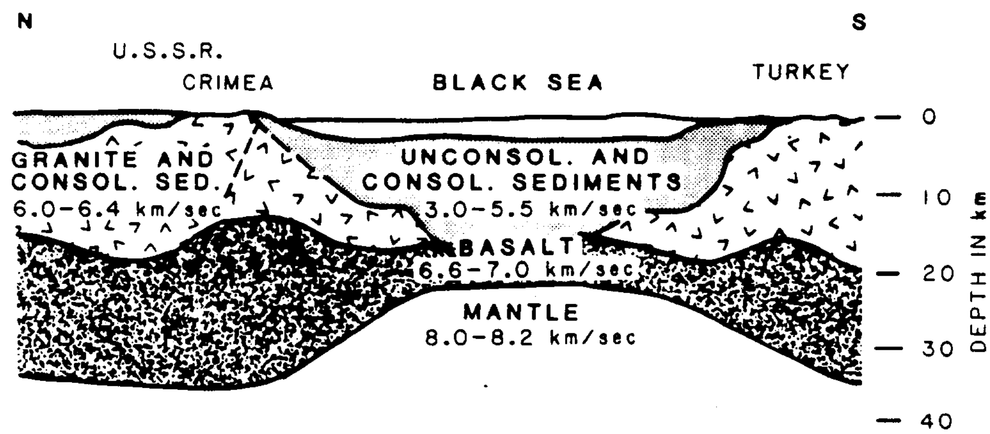


Figure 6. CRUSTAL NORTH-SOUTH CROSS SECTION ACROSS THE BLACK SEA

Adapted by Ross et al., 1974 from Subbotin et al., 1968; Neprochnov, 1968; Neprochnov et al., 1970

In Brinkmann's hypothesis, the Black Sea basin was initiated by a long period of uplift and erosion resulting from crustal lateral tension. Increased thickness of suboceanic crust caused the formation and sinking of a "soft" mantle. Subsequent decreased temperatures of the crust and mantle resulted in increased subsidence of the basin and the cessation of volcanic activities. During the process of increased subsidence, the basin was being filled with sediment.

Seismic activity is usually a good indicator of tectonic stability of an area. In the Black Sea, the present seismic activity is shallow and is restricted to the southern marginal zones of the area. One such zone where the focal depth is less than 30 km extends along the onshore Anatolian Fault which strikes parallel to the southern flanks of the Black Sea basin (Canitez and Toksoz, 1970). Another shallow seismic zone has been identified in a southwest direction from the eastern Black Sea across the Caucasus Mountains into the Caspian Sea and south-central Asia (Nowroozi, 1971).

Lithostratigraphy

Knowledge of lithostratigraphy of formations in a study area constitutes one of the major elements in the assessment of gas hydrate formation and stability potential. The related lithostratigraphic factors range from a sediment's thermogenic hydrocarbon generation potential, heat flow alteration, and generation of a chemical reducing environment needed in the process of biogenic methanogenesis, to the favorability of lithologic strata as a gas hydrate host formation.

Contemporary knowledge of lithostratigraphy of the Black Sea is based on data obtained from DSDP holes at sites 379, 380 and 381, drilled during the Glomar Challenger cruise (Figure 7). Most of the penetrated sequences were found to be of Quaternary age, which in the central part of the basin exceed 1,000 m in thickness. The oldest sediments, of Miocene age, were probably encountered at Site 381 (Ross et al., 1978). The lithostratigraphy of the recent sediments has been studied based on shallow penetrating piston cores.

DSDP Site 379

This DSDP hole is located in the abyssal plain of the Black Sea (Figure 1) and was continuously cored to a depth of 624 m. The oldest recovered sediments were of Pleistocene age. Lithologically the whole sedimentary sequence at DSDP Site 379 can be generally considered as one unit composed of dark greenish-gray terrigenous mud. The alterations within predominant muds consist of silty clays to clayey silts with intercalations of thin sandy silt and sandy laminae. Locally, the silty and sand beds were found to be up to 8 cm thick. The sediments consist mainly of quartz, feldspars, clay minerals, detrital carbonates and smaller amounts of pyrite, heavy diatoms, nannofossils, and organic matter. Smectite and illite with small amounts of chlorite and kaolinite are the dominant components of the clays. The average content of carbonates in vertical profile of the hole was found to be rather low

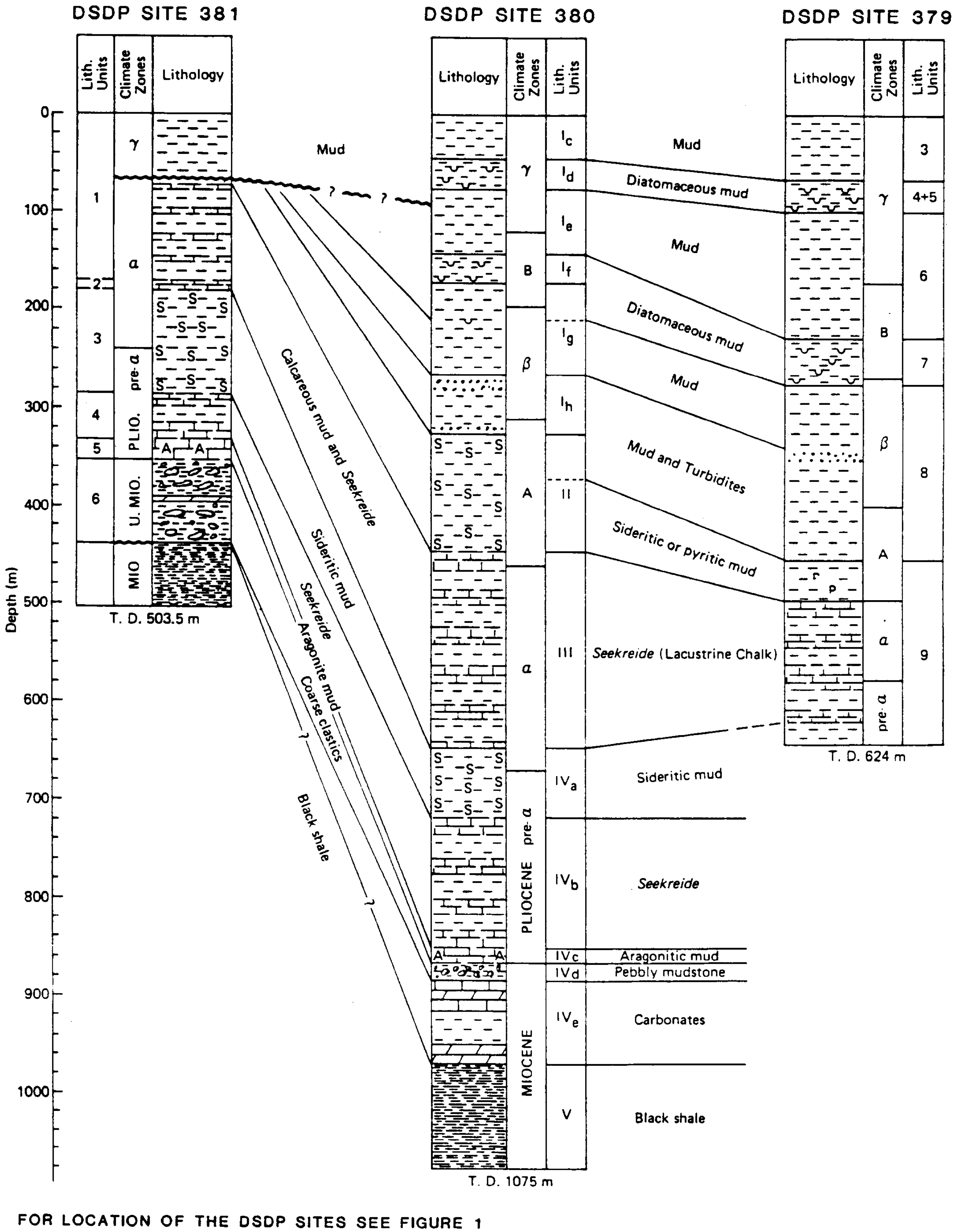


Figure 7. CORRELATION OF LITHOLOGIC UNITS BETWEEN THREE BLACK SEA DSDP SITES

After Ross et al., 1978

(approximately 15%), represented mainly by calcite and traces of dolomite. Distribution of the carbonates indicates their higher concentration in lower sections of the profile where bands rich in carbonates contain up to 60% $CaCO_3$. The latter implies the significance of chemical sedimentation in deeper parts of the profile. Indigenous fossils of diatoms, foraminifers and nannofossils appear to be generally rare and restricted to certain intervals.

Based on lithology, nine units were discerned in a sedimentary sequence at DSDP Site 379 (Figure 7).

Unit 1 (0-0.30 m) is represented by nannofossil ooze. The presence of this unit was extrapolated from piston cores recovered in the vicinity of DSDP Site 379. These sediments were deposited at present marine conditions of the Black Sea.

Unit 2 (0.30-0.70 m) is also known only from piston cores. It consists mainly of sapropel (containing approx. 40 to 50% organic matter). The water content in the unit is in the order of 90%. Occasional thin nannofossil beds and fine layers of inorganic aragonite were also found within this unit. The sediments of Unit 2 reflect an environment devoid of oxygen with a well developed H_2S zone. Such conditions originated in the Black Sea about 7,000 years ago.

Unit 3 (0.70-65 m) is mainly composed of terrigenous muds. Silt and fine sand occur in subordinate amounts and form streaks and patches, and occasionally layers. The graded bedding of these components has been suggested to represent turbidites (Ross et al., 1978). Clays are represented by illite and smectite and to a lesser degree by chlorite and kaolinite. Quartz and feldspar often constitute more than 30% of the sediment mass. The average carbonate content was found to be approximately 15%. The major heavy minerals, pyroxene, epidote and green hornblende are thought to indicate a southern and southeastern source area. The nannofossils found in this interval represent reworked material of Cretaceous and Tertiary age. The diatoms identified in cores are indicative of a fresh-water environment, probably reflecting the time when the Black Sea did not have a water connection with the Mediterranean Sea.

Unit 4 (65-100 m). This unit is represented by a dark greenish-gray mud. The upper boundary of this sequence was delineated on the basis of the first appearance of marine diatoms, foraminifers, and nannofossils beneath the sediments of Holocene age. Within Unit 4, short fresh-water periods are marked by intercalations of thin layers containing fresh-water diatoms.

Unit 5 (100-100.3 m) consists of an intensely compacted layer of sapropel where organic matter content may reach 15%. Thin white layers within that interval are composed of nannofossils or aragonite. Both type of sediment and type of nannofossil indicate brackish stratified water conditions in the marine environment.

Unit 6 (100.3-225 m) is composed mainly of greenish-gray terrigenous mud. The major components are quartz feldspar and detrital carbonates. In the lower sections of this unit, layers of silt and sand deposited in cycles of 10-15 cm were identified. The diatoms found indicate an all fresh-water depositional environment, with the exception of the 161-168 m interval, which represents a short marine sedimentary episode.

Unit 7 (225-275 m) is composed of a diatomaceous nannofossil-rich terrigenous mud. The characteristic feature of this unit is the presence of diatoms and nannofossils in different layers as well as the first occurrence of authigenic carbonate. Several thin sapropelic horizons were also encountered in this unit. Authigenic carbonates occur in 3-7 cm thick light gray massive layers. The carbonate content in these layers is up to 74% and is represented by calcite. Similar carbonate rocks are known from perialpine lakes as "seekreide", indicating a fresh-water environment. Layers of sandy silts often present in this interval are probably of turbidite origin.

On the basis of nannofossil and diatoms found in Unit 7 as well as on the type of sediments it has been concluded that most of them were deposited in brackish-marine water conditions with various degrees of oxygenation.

Unit 8 (275-453 m). The sediments in this unit are mainly dark greenish-gray terrigenous muds similar to those in units 3 and 6. Except for turbidites with a rhythmic pattern of 7-10 cm thick, light gray sandy silt and silt layers, occasionally showing cross-bedding and ripples, were found in Unit 8. Abundant carbonate rock fragments were identified in the silt layers along with different heavy minerals (opaques, garnet) than those found in turbidite layers (epidote, green hornblende, pyroxene). The silt layers were interpreted as loess deposits (Ross et al., 1979). At the same time, no indigenous fossils were found in the sedimentary sequence of this unit.

Unit 9 (453-624 m). Although the sediments of this unit also consist mainly of terrigenous muds, the presence of intercalated carbonate-rich layers with a characteristic rhythmic sedimentation pattern differentiates Unit 9 from the previous Unit 8. The pattern is mostly represented by a repeated sequence of pyrite, dark clay and calcite. Usually these sequences are 3-6 cm thick. From the bottom up, each sequence starts with a 2-3 cm thick layer of pyrite, which is followed by dark clay which grades into a gray clay. White to yellowish fine-grained carbonate mud is the uppermost element of the sequence. Finely dispersed pyrite has been found throughout the dark and gray sequences. The boundaries between all components of the sequences were always found to be sharp. Overall, the dominant lithologies in Unit 9 are terrigenous muds composed of quartz and feldspar (up to 25%), and clay minerals and detrital carbonates composed of calcite and traces of dolomite. The repeated depostional variations in Unit 9 are not well understood. While the fluctuations related to the seasonal climatic cycles must be discarded, changes of thermocline in the water column have been suggested as the major factor (Ross et al., 1979). There is a general lack of indigenous fossils in Unit 9.

DSDP Site 380

DSDP Site 380 is located in the extreme southwestern part of the Black Sea, near Bosporus, on the basin apron (Figure 1), in a water depth of 2,107 m. The drilling of two closely spaced holes made it possible to obtain an insight into the sedimentary sequences to the maximum subbottom depth of 1,073.5 m. The choice of moving the site location toward the flank of the basin near Bosporus was motivated by the possibility of reaching sediments older than Pleistocene. During the Pleistocene, the Bosporus constituted the only connection with the Mediterranean Sea. Since the sedimentation in the Black Sea basin seems to have been strongly related to the closing and opening of the natural connection with the Mediterranean Sea, the lithological profiles close to Bosporus should contain the best record of the changes of the sedimentological regimes. A characteristic feature of the lithological profile at Site 380 compared with the deep-sea sequences is the small percentage of biogenic components. At the same time the chemical sediments constitute a significant portion of the lower half of the lithological profile. Using such criteria as color, grain size, composition, sedimentary structures, occurrence of chemical sediments, unusual minerals, fossils, enabled Ross et al. (1979) to distinguish five major lithological units and subunits in the profile of DSDP Site 380 (Figure 7).

Unit 1 (0-335 m) represents terrigenous sediments and consists of muds, silts and sands. Mineralogically, these lithological components are quartz, feldspars, clay mineral, detrital carbonates, pyrite, organic matter diatoms, and heavy minerals. Most of the sediments in this unit have been classified as muds. The muds are mostly composed of clay minerals (illite and smectite) with subordinate amounts of silt-sized quartz and feldspar grains. Sandy silts and sands were interpreted as being of turbidite origin. Small amounts of detrital carbonates (traces to 20%) are present throughout the unit. Chemical sedimentation was insignificant during the time corresponding to deposition of Unit 1.

Unit 2 (332.5-446.5 m). The unit was found to be mostly a mud sequence intercalated with numerous carbonate-rich layers. The mud is composed of quartz, feldspars, clay minerals and minor amounts of detrital carbonates. The color of these sediments varies from greenish-gray to olive-gray and dark greenish-gray. While darker muds are rich in pyrite, the light colors reflect higher content of diatoms and carbonates. With regard to the grain size, fractions less than 2 m were found to constitute more than 65% of the bulk. The smallest fractions of terrigenous clastics were represented by varved clays. The varves are interbedded with structureless gray marls. The pale brown color of the varve intervals seems to indicate the presence of iron in a ferric state, thus indicating less anoxic conditions than those which are presently occurring in the Black Sea. Additionally, burrows in these sediments confirm the interpretation of the oxygenated sedimentary environment.

Sandy silts constitute a very limited type of sediment and are scattered in a form of thin laminae throughout Unit 2. Three types of chemical sediment have been identified. Siderite-rich marls are present throughout the whole unit in the form of thin layers (up to a few cm) and laminae. Calcareous ooze represents similar sediment to the carbonates found in perialpine lakes in Switzerland and where the term "seekreide" for lake chalk was adopted. Calcite is usually the major component in seekreide and may constitute as much as 80% of the sediment bulk. Aragonite is present in Unit 2 as a chemical precipitate or as an authigenic product in the mud near the top of the unit.

The depositional environment for Unit 2 appears to have been marine-brackish for the uppermost sequences. On the other hand, the oldest sediments of the unit were deposited in a fresh or only slightly brackish lake. The sedimentary facies between the two mentioned sequences represent oscillating conditions between the one which produced seekreide and the one favorable for siderite formation.

Unit 3 (446.5-644.5 m). Muds, marls and seekreide constitute the dominant lithologies in Unit 3. Below the subbottom depth of 540 m, cyclically deposited beds observed above seekreide in Unit 2 are absent. Instead, carbonate varves occur in the form of thin laminations. The latter sediment consists of light olive-gray calcareous ooze composed of $CaCO_3$ (75-80%) and organic-rich clays or marls. Within the upper 40 m of Unit 3, the cyclically deposited calcareous oozes are horizontally layered. Below this section the sediment reveals features of slumped masses divided by horizontally deposited sediments. The slumping processes are extremely probable in view of the presence of relatively great amounts of the seekreide (i.e. calcareous lacustrine chalk) which is known for its lack of stability and common phenomenon of subaqueous slumping. Fauna assemblages (particularly ostracode fauna) found in the sediments of Unit 3 suggest a deep fresh-water depositional environment for these sequences.

Unit 4 (644.6-969 m) features quite a variety of sediment types, which also include different chemical sediments. The uppermost 70 m interval of this unit is predominantly diatomaceous clay. Numerous manganosiderite intercalations were found within this interval, contrary to the siderite in soft marls and muds occurring in Unit 2. The siderite sediments in Unit 4 are invariably hard. The sediments rich in siderite have a pale olive color and occur as thin layers or as nodules. Clay beds consist mainly of clay minerals with various amounts of diatoms ranging from 15 to 60%. Carbonate minerals, with the exception of minor traces of detrital carbonates, are absent in the clay beds. A few layers of light olive-gray diatomaceous seekreide were found at the top of Unit 4.

Based on the type of sediments and diatom assemblages it has been concluded that the upper 70 m of the sedimentary sequence in Unit 4 was probably deposited in an environment oscillating from fresh to brackish.

The 718-850 m interval is represented by three major components: terrigenous clays, calcite and diatoms. In the absence of manganosiderite, the seekreide is an important constituent. All these components occur in various proportions in laminated and structureless sediments. The sediments in this interval were deposited during a period of time with significant precipitation of calcite. Diatom assemblages indicate a change from a marine-brackish to more fresh-water environment during this time.

The 850-864.5 m interval differs from the overlaying sedimentary sequences by the presence of aragonite and magnesian calcite as chemical sediments. Olive to black diatomaceous shales constitute the dominant lithology. Some of the sediments do not contain carbonates whereas some are marly with 10-20% $CaCO_3$. The diatomaceous shales are intercalated with aragonite. The sediments of this interval were deposited in a brackish marine environment.

Immediately below the above described group of sediments was found the most unusual lithological sequence in the Black Sea. The 864.5-883.5 m interval is constituted of pebbly mudstones, stromatolitic dolomites and cobble clasts of conglomerate. The most indicative for a sedimentary environment are stromatolitic dolomites which are characteristic for intertidal to supratidal shallow marine zones. The dominant lithologies in this depth interval are conglomerates, slump breccias, or pebbly mudstone. As these deposits consist mostly of dolomite, their origin is not certain.

The 110 m thick bottom interval of Unit 4 (838.5-969 m) is characterized mainly by the presence of dolomite in a laminated sequence of seekreide and marls. The dominant lithologies are greenish-gray calcareous muds or marls. Intercalated in structureless marly sediments are aragonite calcite and dolomite. The sediments of this interval were probably deposited in a shallow fresh-water environment.

Unit 5 (969-1073.5 m) is represented by black shales, zeolitic sandstones and dolomite. The transition from Unit 4 to Unit 5 is marked by intercalations of light and black varves.

The "black" shales are greenish-black and fissile. They consist of clays, organic matter, and contain up to 20% quartz and feldspar, 10% pyrite, but no carbonates. The dolomite intercalations consist of almost pure dolomite and occur either in the form of laminae several centimeters thick or as layers a few centimeters thick. Quantitatively, dolomite is insignificant because it constitutes less than 1% of the cored interval. Zeolitic siltstones and sandstones in Unit 5 are tuffaceous with laminae stratification or grading. Typically, a graded bed is a few centimeters thick.

DSDP Site 381

Site 381 was drilled in the Black Sea slope southwest of Site 380 (Figure 1). The water depth at the site is approximately 1,728 m and the hole penetrated 503.5 meters of sediment. However, only 269.5 m of cored sedimentary sequence were recovered. Because of the location of Site 381, it is believed that the lowermost recovered core represents the oldest sediments known in the Black Sea basin. These sediments have been assessed on the basis of pollen data to be of upper Miocene age. Shipboard and onshore laboratory examination of the recovered sediments enabled the detection of nine lithological units in the profile of Site 381 (Figure 7).

Unit 1 (1-171 m) is composed mostly of bluish-gray to greenish-black terrigenous mud. Examination of pore water and palynological data from sites 380 and 381 indicated that much of the upper terrigenous section is missing. The explanation of this fact is the position of the site on the continental slope where removal of sediments can be quite extensive. Mineralogically, the sediment in Unit 1 is mainly composed of clay minerals (illite, smectite, kaolinite, and chlorite), quartz, feldspar, detrital carbonates (calcite and smaller amounts of dolomite), and some heavy minerals. Average content of carbonates does not exceed 17%. The heavy mineral assemblage which includes epidote, hornblende, and garnet suggests the Danube origin for the sediments. Marine diatoms were found only in the upper section of the unit.

At the same time, no indigenous nannofossils were reported from this interval. Medium-gray silty sand composes the bottom 10 m of Unit 1. The major components of the sand are mollusc fragments and well rounded quartz and feldspar grains. The size (300-500 m) and good sorting of the sand grains is characteristic of a beach depostional environment.

Unit 2 (171-173 m) is represented by a 2 m thick interval of seekreide. Only slight indications of a cyclic sedimentation pattern (2-5 cm) were marked by dark greenish-gray and lighter greenish-gray layers. The lighter colors indicate a higher carbonate content (up to 57%). The carbonate mineral content is mostly calcite. Again, the correlation of these deposits with Site 380 suggest the presence of an unconformity where a significant portion of the original sediment has been erosionally removed.

Unit 3 (173-285 m) consists of a dark greenish-gray to olive-gray diatomaceous sapropelic mud. The unit is mostly composed of clay minerals, quartz, feldspar, siderite and diatoms. Compared to Units 1 and 2, a significantly higher content of smectite was observed in Unit 3. Fresh-water diatom content was also found to be relatively high (up to 25%). Besides diatoms, siliceous spicules and fish bones were commonly identified. With the exception of siderite and manganosiderite, carbonates rarely occur in this unit. This is most likely due to the fact that the calcium carbonate becomes chemically unstable at times of sapropel formation. Two layers, 3 to 5 centimeters thick, of manganosiderite occur throughout the unit.

Unit 4 (285-323 m). This unit is composed of pale olive diatomaceous carbonates. The most prominent feature which distinguishes Unit 4 from the previous one is the higher amount of calcite (up to 80%) and smaller amount of diatoms (<15%). Sediments in Unit 4 show a finely laminated pattern which resulted from fluctuating amounts of deposited calcite, clay, and diatoms. Besides fine laminae, 4 cm thick beds of carbonaceous sediment with abundant burrows were also found. The identified diatoms were interpreted by Schrader (1978) as marine.

Unit 5 (323-352 m) is composed of an olive-gray diatomaceous sapropelic mud intercalated with finely laminated carbonates. The carbonates are represented by needle-shaped crystals of aragonite and to a lesser degree by Mg-calcite. The sapropelic mud is devoid of carbonates whereas the average diatom content is 30% and organic carbon reaches 6%. Diatoms found in this unit are characteristic of a brackish-marine sedimentary environment.

Unit 6 (352-437 m). Recovery of the core from this interval was only 10%. Therefore, only a sketchy lithological profile could be derived. Unit 6 consists of a mixture of pebbly mudstone, breccia shell hash, sand, and mud. Angular fragments of dolomite were commonly found in mud sections. Analyses of the dolomite fragments indicate the depositional environment of shallow supratidal water. A marine environment of sedimentation has been confirmed by marine diatoms.

Unit 7 (437-465 m) is represented by an olive-gray to olive-black, finely laminated siltstone, rarely interbedded with thin silty sand layers. While there is an abundance of quartz and feldspar, no carbonates were found in Unit 7. The clays are dominated by smectite. The content of organic carbon was found to be about 1%. Identified fish remains as well as the type of diatoms is probably indicative of a fresh-water environment.

Unit 8 (465–475 m) is composed of a breccia which features an abundance of soft sediment deformations. The clasts vary in color from olive-gray to lighter gray in sections richer in carbonates. Sediment in this unit consists of clay minerals (mainly smectite), quartz, and feldspar.

Unit 9 (475-503 m) features mainly dark greenish-gray finely laminated siltstone. Although the sediments in this unit are very similar to those in Unit 7, small bands of siderite are presesnt. The maximum thickness of these bands is 2 cm. No carbonates were found in Unit 9.

Sedimentation

Although the deepest directly analyzed sediments from the Black Sea basin are from 1,074 m subbottom depth (DSDP Site 380), the geophysical studies have shown that as much as 17,000 m of sedimentary sequence may overlie the basaltic basement in the central part of the basin. It appears, therefore, that the sedimentation in the Black Sea basin has lasted for a considerable length of time, estimated at 300 m.y. (Brinkmann, 1974; Hsu et al., 1977). As only a small portion of the younger sediments are directly known, the sedimentary environments older than upper Miocene still remain quite obscure. The difficulties in even general approximations are due to persisting controversies within such basic areas as the tectonic position and age of the basin. Among the important questions pertaining to the sedimentation is the bathymetry of the basin, which delineates to a significant degree the boundaries and types of lithofacies. Deeper reflectors on seismic profiles from the Black Sea show features which indicate a process of slumping of large masses of sediment from the shelf and slope areas out to the deeper parts of the basin (Neprochov and Ross, 1978; Figure 8). On the other hand, some authors (Schrader, 1978; Degens et al., 1978; and others) argued that while the entire Black Sea region was much shallower prior to Pleistocene time, it has been subsiding since about Cromerian (Pleistocene) time. The arguments of the latter group of authors are based on features of subaerial exposure and probable erosion of sediment found at Site 381 (the present position of this interval is at approximately 2,150 m below sea level). Also, the sediments of a shallow water environment were found at Site 381 where their current depth is approximately 3,000 m below sea level. These data, in the opinion of the above mentioned authors, indicate the possibility of 2,000 to 3,000 m of subsidence of the Black Sea region since early Pleistocene. An equally logical alternative to the scenario involving the subsidence processes is the idea of the fluctuating basin water level (Hsu, 1978).

Although the idea of subsidence cannot be totally discarded, low probability for recent large-scale downward movement along fracture zones of sediments can be questionable in view of the two arguments proposed by

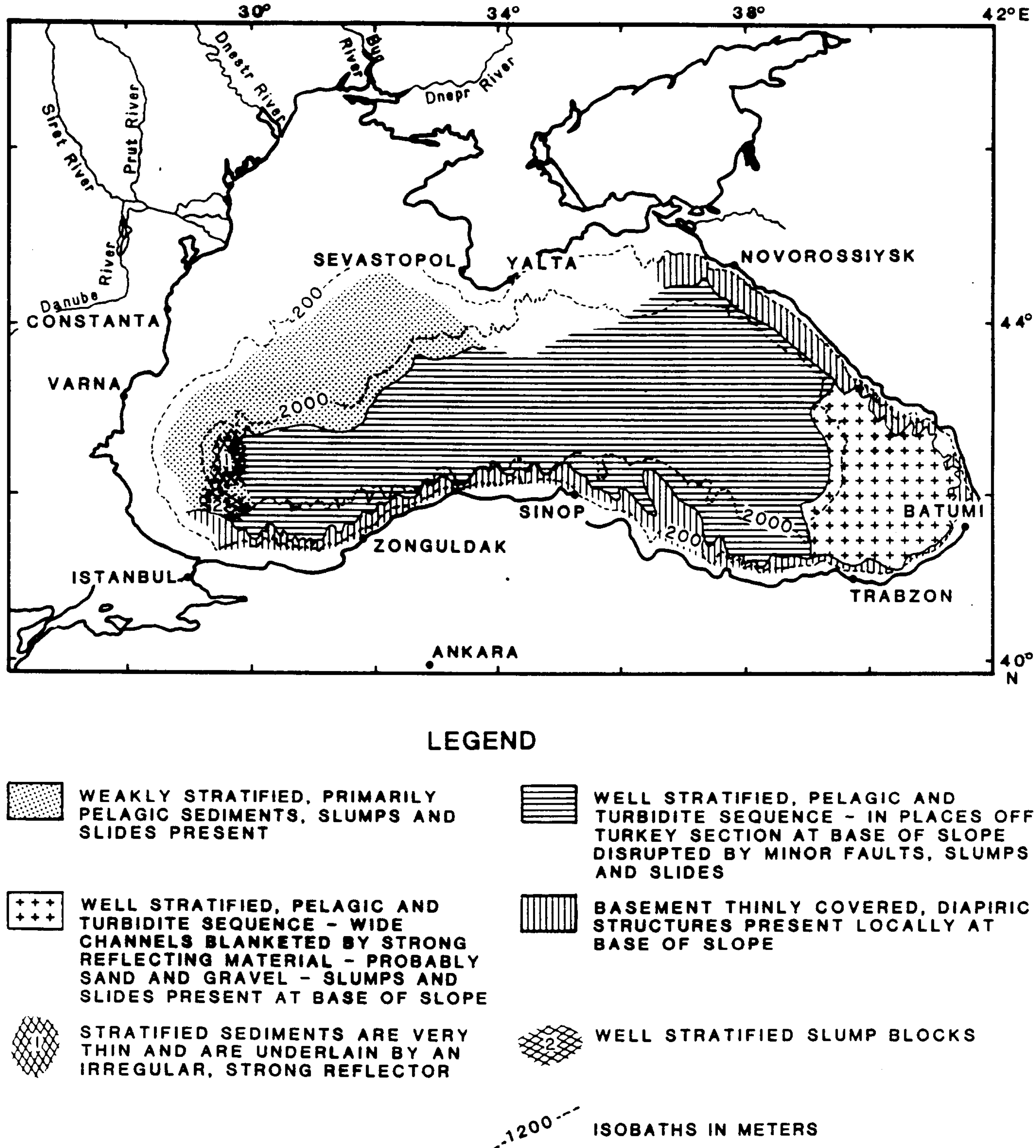


Figure 8. STRUCTURAL FEATURES OF THE BLACK SEA BASED ON SEISMIC PROFILES OBTAINED DURING 1969 ATLANTIS II CRUISE

After Ross et al., 1974

Neprochov and Ross (1978). One of these arguments calls for the lack of downfault features on the deep-penetrating seismic lines from the region. The other argument points at a general lack of large-scale earthquakes in the region.

Based on geophysical evidence as well as on a variety of petrological and geochemical data, the changes of the sea level appear to be a major factor which influenced the sedimentation in the Black Sea region.

The fact that the Black Sea is a closed basin where the Bosporus is the only water communication to larger marine environments seems to have played a prime role in establishing sedimentary environments, at least throughout the Quaternary history of the basin (Figure 9). At the present time, the seal separating the Black Sea from the Sea of Marmara is only 50 m below the water level. The lowering of the sea level during the Quaternary period effectively shifted the aqueous environment toward a fresh-water type (Degens et al., 1978). Conversely, the increase of the sea level caused spills of the salty marine waters into the Black Sea. The most important consequence of the latter events was the formation of the anoxic zones which greatly influenced chemical and biochemical sedimentation as well as the deposition of terrigenous material.

Review of the lithological profiles from the DSDP sites in the Black Sea indicate that in late Tertiary-Quaternary sedimentation in the Black Sea basin, three stages of depostion took place:

a. black shale depostion,
b. periodic chemical deposition,
c. terrigenous deposition.

Black Shale Deposition

Black shales represent the oldest penetrated sediments in the Black Sea (DSDP Site 381). The intercalated layers of pure dolomite which constitute 1% of these sediments occur with increased frequency toward the top, indicating transition to a stage of chemical sedimentation. Although the black shale strata contain some detrital carbonates (10% or less), they are devoid of autochthonous carbonates with exception of the occasional dolomite formation which occurred during arid periods when the Black Sea water reached supersaturation due to intensified evaporation.

The understanding of the depositional processes of organic-rich sediments was significantly improved through a detailed organic geochemical analysis of a Black Sea sapropel and work by Deuser (1974). These studies showed that sapropel formation starts shortly after saline water enters a fresh-water basin. Even initially established pycnocline and halocline reflect stratification in the water column, which eventually leads to water stratification where an upper oxygenated zone and lower anoxic zone are present (Figure 10). Anoxic conditions can usually be established within a few years. A permanent halocline is established at a certain depth delineating the boundary between anoxic and oxygenated zones. Such a chemical interface rises in response to the continuing supply of salt water. Subsequently, the anoxic layer is enlarged vertically and horizontally.

Lack of calcium carbonates in the black shales is also characteristic for anoxic environments. Such a relationship has been observed in many sediments of reduced environments (Exon, 1972). Carbonates delivered to the

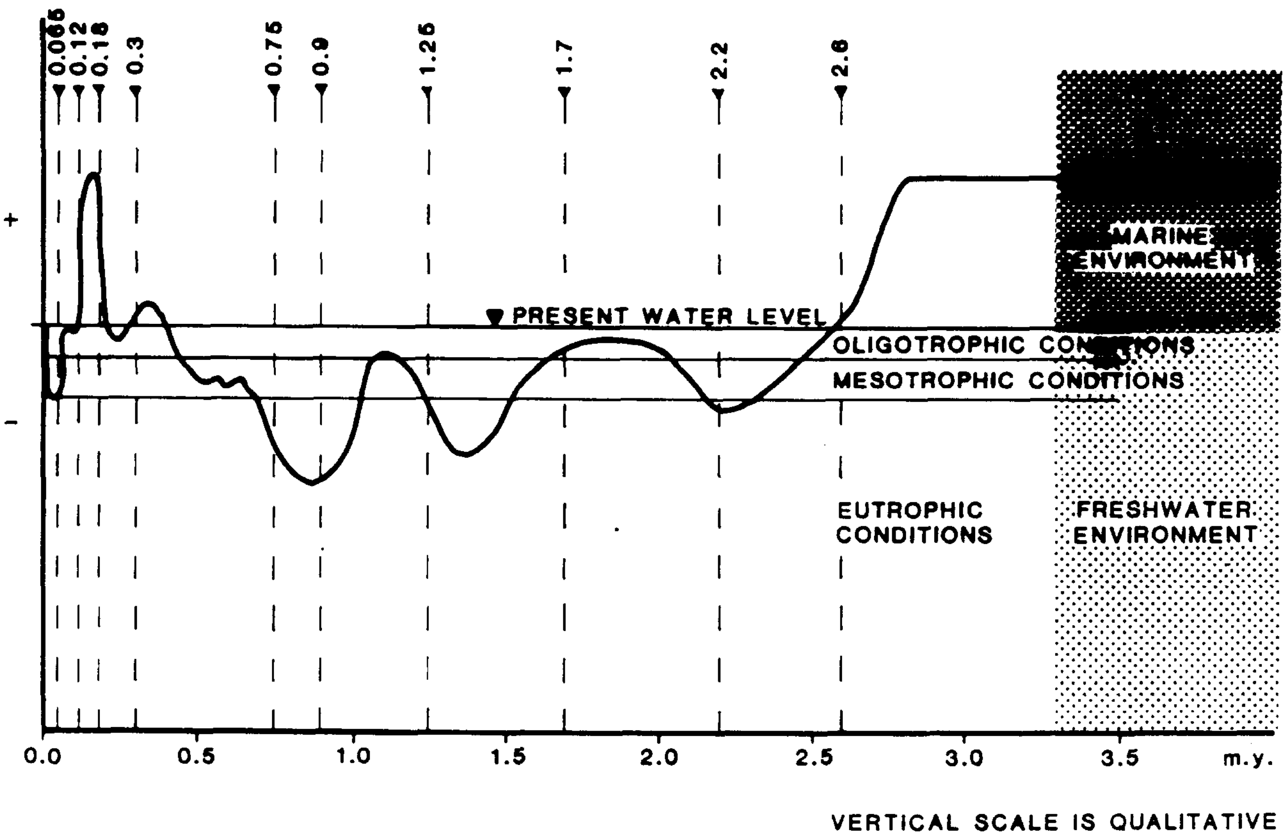


Figure 9. PAST SEA-LAKE-LEVEL CHANGES IN THE BLACK SEA BASED ON DIATOM FLORAL CONDITIONS

After Schrader, 1979

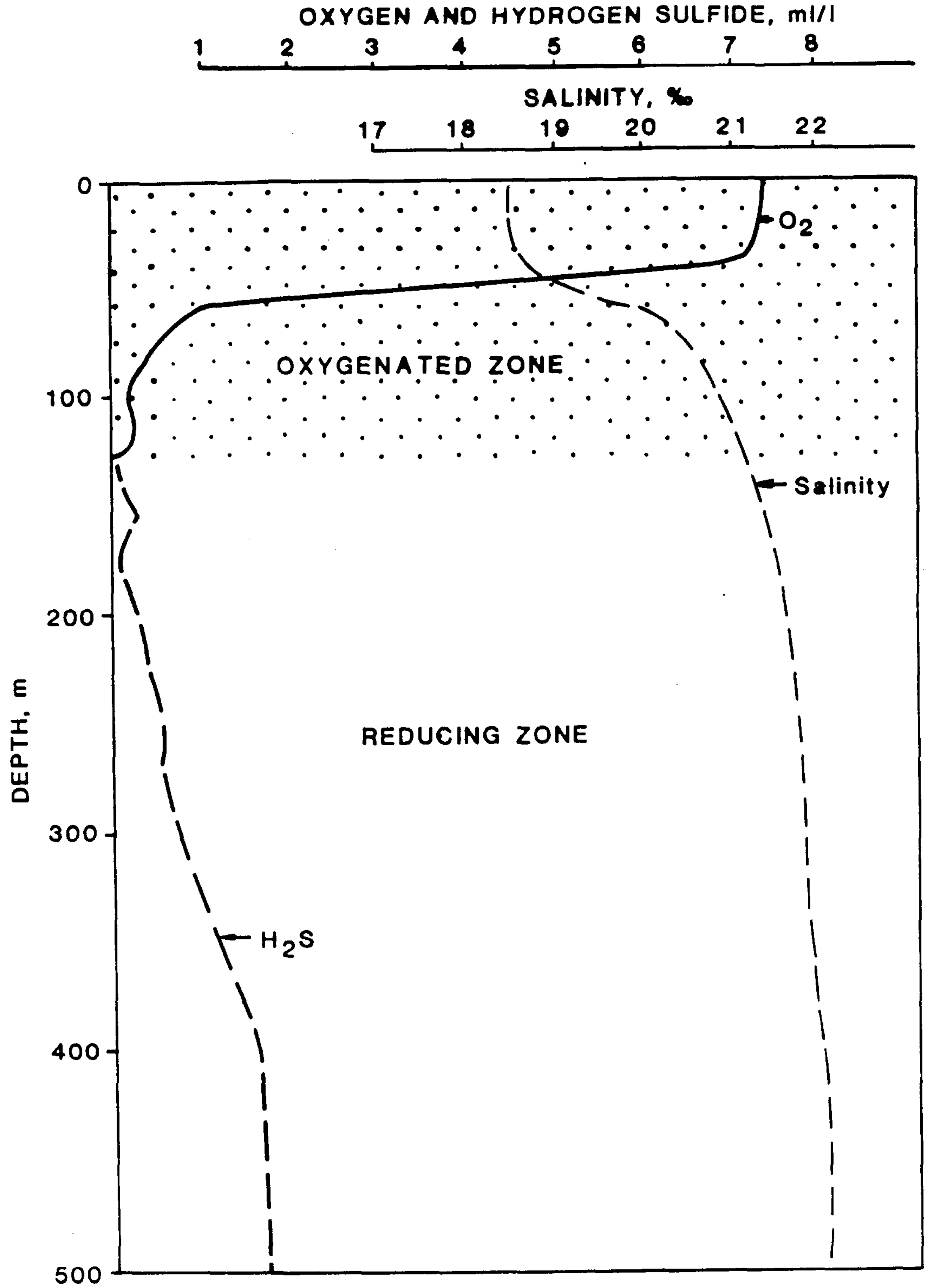


Figure 10. VERTICAL DISTRIBUTION OF SALINITY, OXYGEN (O_2), AND HYDROGEN SULFATE (H_2S) AT STATION 1466 IN THE BLACK SEA

After Degens et al., 1980

anoxic basins are dissolved by carbon dioxide, which is the product of the decay of organic substances within the sediments (Figure 11). Contrary to the anoxic environment, carbonates are preserved under oxic conditions which coincide with an environment poor in organic matter. The described pattern, related to a vertically moving interface between oxygenated and reducing zone, is shown in Figure 11.

Chemical Deposition

These sequences overlying black shales coincide with Unit 4 at Site 380 and consist of such elements as dolomite, aragonite calcite, magnesian calcite, and manganosiderite. The accumulation of such sediment could have occurred mainly because of the low input of terrigenous material into the basin. A significant reduction of terrigenous influx in Holocene time is believed to have occurred due to climatic conditions during warmer periods of time when the sea level rose and most of the detritus from land was retained in marginal parts of the basin (Ross and Degens, 1974). The fact that the Neogene chemical sediments were deposited both in warm and cold climates implies that other than climatic conditions were causing low terrigenous influx. Hsu (1978) suggested that until a major reorganization of the river system which diverted major rivers to the Black Sea, a relatively insignificant amount of terrigenous detritus was transported into the basin.

Muds and clays are dominant lithologies in the sequence interbedded with chemical sediments. The alternating carbonates and muds or clays are thought to be a result of precipitation cycles known from contemporary sediments of Swiss Lakes, i.e. terrigenous sedimentation prevails during wet years while carbonate (seekreide) is deposited during times with limited rainfall.

The chemistry of the water in the ancient Black Sea is commonly credited for the various types of carbonate precipitates (Hsu, 1978). Studies of sediments from modern lakes revealed that the diversity of calcium carbonate mainly depends on the Mg:Ca ratio in the lake water. A ratio value less than 1 results in calcite precipitation. Increased values of the ratio yield magnesian calcite and then aragonite. While river water usually has a low Mg:Ca ratio, the indispensable magnesium concentration in the Black Sea could have increased as a result of evaporation with earlier preferential precipitation of $CaCO_3$ or by supply through the seawater influx. The presence of marine brackish organisms in the sediments seems to favor the latter source of magnesium.

The explanation of the genesis of dolomite is somehow difficult while it is not fully understood. Association of the dolomite intercalated with black shales as well as in sequence with aragonite and calcite suggest chemical precipitation. At the same time, the presence of stromatolitic structures in some dolomite sections suggests a replacement origin typical of supratidal environments. The provenance of siderite in the sequence of chemical sediments is even more obscure and difficult to explain. According to Berner (1971), the precipitation of siderite requires an environment where the ratio Fe:Ca is higher than 0.05 and the concentration of sulfate ions must be low enough to prevent pyrite precipitation. Diatoms found in the sediments indicate a brackish environment, while the only conceivable depositional environment would be the one where increased salinity was caused by

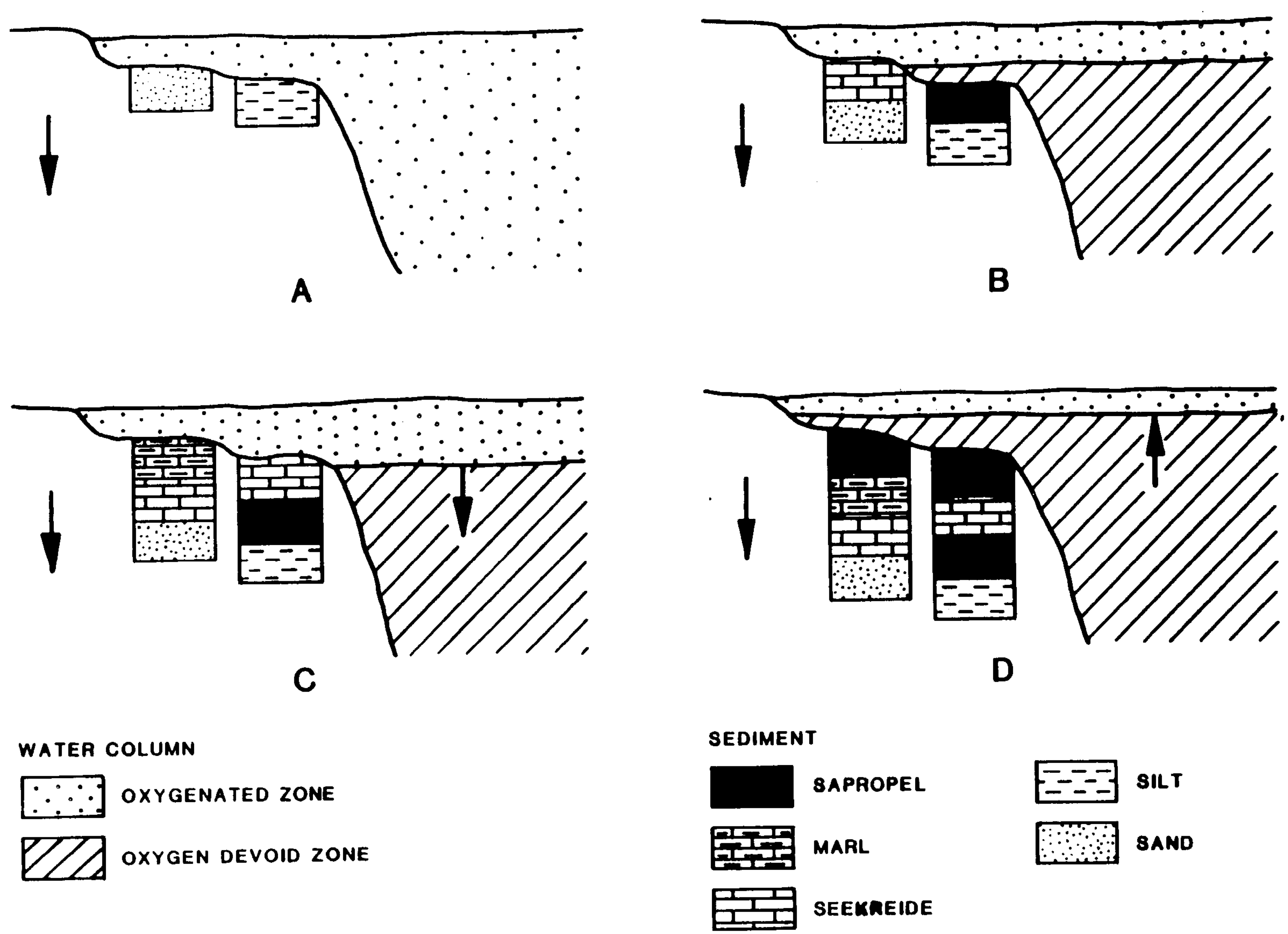


Figure 11. FORMATION OF STRATIFIED WATER AND RELATED SEDIMENTATION IN THE BLACK SEA

After Degens et al., 1980

excessive evaporation. After carbonate sedimentation, establishment of anoxic conditions, and under limited supply of the sulfate ions from the Mediterranean Sea, sedimentation of siderite could have taken place.

In summary, it can be concluded that deposition of the chemical sequences in the Black Sea region was closely related to the fluctuations of the sea level, influx of terrigenous material, and climatic conditions.

Terrigenous Deposition

Initiation of terrigenous deposition is noticeable in the profile of Site 380 at 320 m subbottom depth. The onset of this sedimentation coincides quite well with the commencement of the glacial stage Beta. Although the changes of sedimentary environment related to glacial stages may have had profound effects on the type of deposition, the continuation of terrigenous sedimentation through interglacial and postglacial periods of time require the involvement of additional factors. Shimkus and Trimonis (1974), and Hsu (1978), suggested that a drainage reorganization, particularly of the Danube River, played a major role in shifting the chemical sedimentation into a terrigenous one. The predominant lithology in the terrigenous complex is muds. Sandy and silty deposits are also present in the form of laminae or thin layers up to a few centimeters thick. Some graded beds have been interpreted as turbidites. The frequency of occurrence of the latter beds is higher at the base of the complex. A characteristic feature of the terrigenous sequences is the almost total lack of chemical sediments corresponding to the interglacial periods of time. The explanation of this fact is probably more complex than models predict (Figure 11), interplay between sea water influx into the basin and climatic conditions defining salinity of Black Sea water.

Recent Sedimentation

Recent sedimentation in the Black Sea is characterized by two major elements: deposition of terrigenous allochthonous material of low carbonate content and large autochthonous production of biogenic carbonate material (coccolithoporid). The annual influx of terrigenous matter into the basin is 2.7×10^8 m^3. Such quantities are the result of the huge drainage area which is approximately 1,864,000 km^2. About 85% of this area represents the Russian Platform whereas 15% is high mountains. The calculations of the solid materials transported to the Black Sea basin show that over 50% of the total influx is being discharged by Danube, Dnestr, Bug, and Dnepr rivers (approx. 1.6×10^8 m^3 per year; Ross et al., 1978). The highest clay and carbonate content has been found in the central areas of western and eastern basins.

Organic Matter

Production, accumulation and preservation of organic matter constitute the major elements in the generation processes of biogenic and thermogenic hydrocarbons. The Black Sea is a unique basin with respect to all three of these elements. Analysis of the contemporary conditions related to organic matter flux may be instructive and applicable to at least a portion of the Quaternary time span when a similar environment existed. As to the contemporary organic carbon circulation in the Black Sea, probably the fullest conceptual and qualitative amount was given by Deuser (1971). The main source of organic matter in the Black Sea is an indigenous process of photosynthesis where the major products are small unicellular algae. It was estimated that about 100 g of organic matter per 1 m^2 during 1 year had been produced by photosynthetic organisms over the Black Sea region during the last 2,000 years. Only a minor amount of organic matter (less than 10%) is introduced to the Black Sea basin in the form of detrital material transported by rivers. According to Shimkus and Trimonis (1974), the latter source of organic carbon amounts to up to 30% of the total input. The third source of organic carbon is originated by processes of chemosynthesis. Although the contribution of this source is not known adequately, it was estimated at less than 15 g of organic carbon per 1 m^2 during 1 year (Deuser, 1971). While oxic conditions prevail in the upper 200 m of the water column in the Black Sea, most of the total organic carbon carried through this zone becomes oxidized and returns to a hydro-atmosphere system. On the basis of calculations of photosynthetic activities, the amount of organic carbon returned to the zones of photosynthesis varies from 80 to 95%. The remaining 5 to 20% reaches the anoxic zone. In the anoxic zone, the organic matter is still subjected to destructive forces, however at a slower pace. It is being oxidized in the process of sulfate reduction, dissolved in water, and the remainder reaches the sediment. Under anoxic conditions, a portion of the organic carbon is used in the process of biogenic methanogenesis, whereas the rest is being buried in sediment. According to Deuser (1974), approximately one fourth of the organic carbon which enters the anoxic zone in the Black Sea is buried in sediments. Such an assumption leads to a simple conclusion that about 4% of the total organic carbon introduced to the Black Sea basin finds its place in bottom sediments. Considering the fact that the average value of organic carbon buried in marine sediments is 1% of the total input, it becomes obvious that the Black Sea represents an unusual type of basin with respect to the amount of organic carbon reaching sediments. It is obvious that the percentage of organic carbon found in recovered cores from the sediments is only partially dependent on the amount supplied to the sea bottom. Permanent anoxic conditions which exist in the Black Sea, where the water depth is greater than 200 m, constitute a major factor in the preservation of organic matter. The ultimate amount of the organic carbon buried in sediment is the net result of the organic carbon supplied and preserved at the sea bottom, biogenic methanogenesis, and the rate of sedimentation. The amount of organic carbon locked and buried in sediments constitutes an important characteristic of hydrocarbon source rock once the sediments enter the oil and gas generation window.

According to Shimkus and Trimonis (1974), the organic carbon content in recent sediments of the Black Sea varies from less than 1% to 5% (Figure 12). The maximum values coincide with the halistatic (oxygen deficient) areas. The analyses of organic carbon in cores recovered at DSDP sites 379 and 380 revealed values of organic carbon ranging from less than 1% to 2% in modern sediments. The data presented by Hirst from shallow piston cores

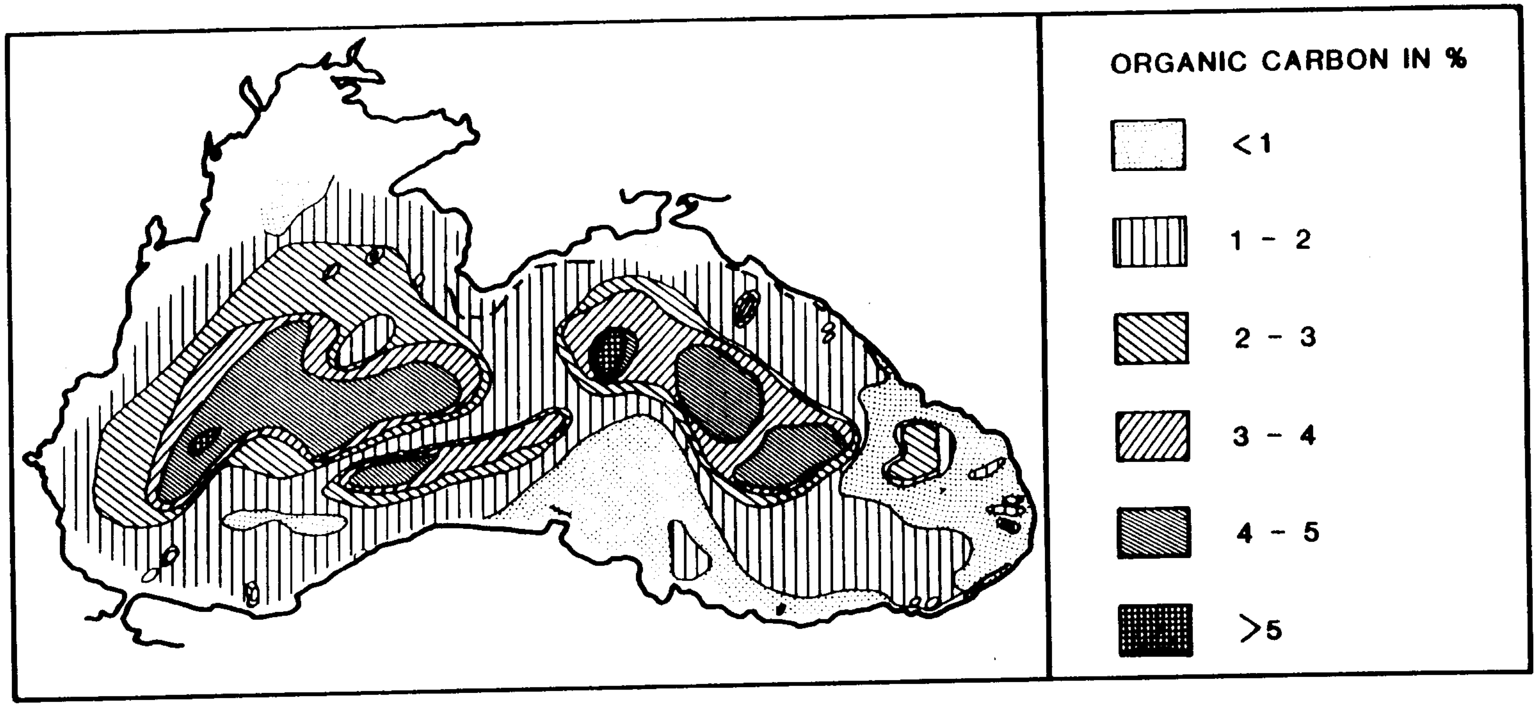


Figure 12. ORGANIC CARBON PERCENTAGE IN MODERN BLACK SEA SEDIMENTS

After Shimkus and Trimonis, 1974

recovered in the central part of the Black Sea (stations 1432 and 1462) show values of organic carbon between 5% and 12.3% (Figure 13). While the latter sediments represent middle Holocene horizons, the organic carbon content in sediments of the middle Holocene does not exceed 1%. In sediments of upper Wurm glaciation period, these values are often below 0.5% (Table 2).

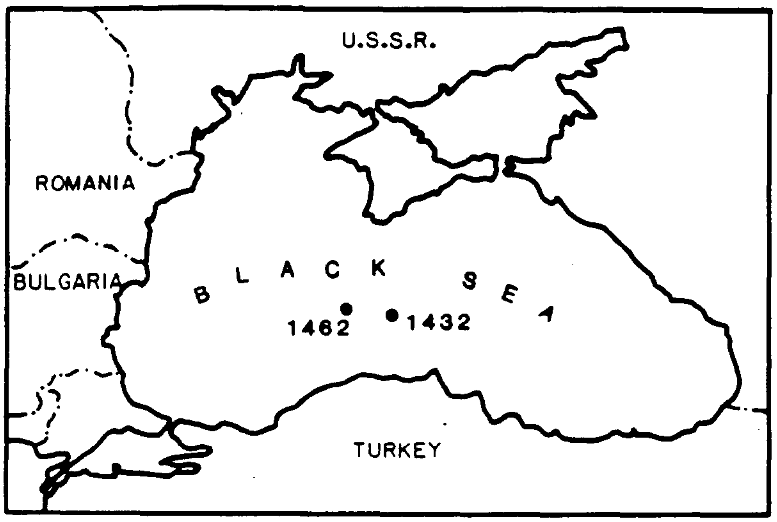
Hydrocarbon Occurrence

Initially the hydrocarbon gases in the Black Sea basin were detected in the sea water column. The first data on hydrocarbon gas in Black Sea waters were published by Atkinson and Richards (1967). These data indicated the presence of methane as a major gas component with trends of increased content with water depth. Similar data confirming previous findings from the Black Sea were presented by Lamontagne et al. (1979). Detailed investigations on hydrocarbon content in deep water sections and nearbottom sediments of the basin carried out by Russian scientists (Tchertkova, 1973; Bagirov, 1975; Tcherednitchenko, 1979; and others) further contributed to the knowledge of hydrocarbon generation processes in the Black Sea basin.

Unique observations and analytical data with respect to hydrocarbons were obtained during part of Leg 42 of the Deep Sea Drilling Project (DSDP) in the Black Sea. The latter data made it possible to establish important relationships based on geochemical characteristics of deeper sediments as well as the pore fluids.

Hydrocarbons in the Water Column

Even a cursory review of the data collected in the Black Sea indicates that methane is the prevailing component of hydrocarbon gas in the water column, usually exceeding 96% of the total hydrocarbons. The methane content in nearbottom sections of the water column in the western Black Sea are shown in Table 3 and Figure 14. The values of methane contents vary from 0.4×10^{-4} ml/l (station 564; Table 1) to 3,422 ml/l (station 601). Sea water saturation in methane appears to be closely related to bathymetry and depth of oxygen-hydrogen sulfate (O_2-H_2S) interface (Figure 15). The highest methane values occur below 50 m with increasing trend downward toward the sea floor. Conversely the lowest methane values ($.5 \times 10^{-4}$ ml/l) were found in shallow shelf areas of the Black Sea. The methane concentration gradient is a major factor causing continuous methane flux upward in the water column. Eventually some methane diffuses into the atmosphere. Although the presently available data do not permit precise quantitative analysis of the methane flux in the water column, some preliminary calculations have been made. Hunt (1974), using values of advective velocity of methane in water = .5 m^2/yr and vertical eddy-diffusion coefficient a = 44 m^2/yr derived by Spencer and Brewer (1971), and applying change of CH_4 concentration over mixing zone +60 to -200 m (relative to (O_2-H_2S interface), obtained a methane flux rate of 47 mL/m^2/yr from the formula:



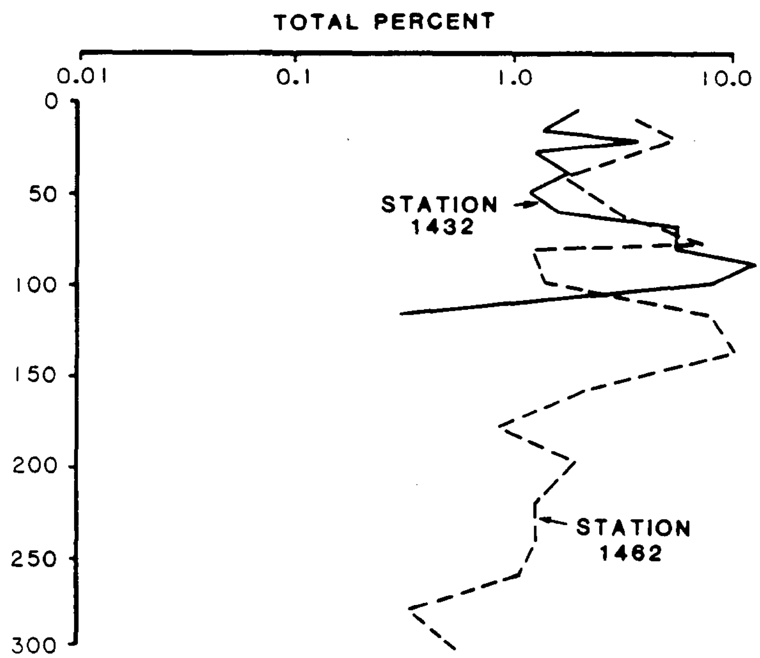


Figure 13. DISTRIBUTION OF ORGANIC CARBON IN VERTICAL PROFILE OF STATIONS 1462 AND 1432 IN THE BLACK SEA

After Hirst, 1974

TABLE 2.

ORGANIC CARBON CONTENT IN PROFILES OF DSDP HOLES 379B, 379A, AND 380A, After Huc et al., 1978

Core	Section	Depth m	Org. C %
Hole 379B			
1	4	4.5	0.41
			0.42
			0.46
			0.45
			0.48
4	4	49.7	0.17
5	3	77.8	0.59
8	3	133.7	0.44
			0.40
			0.43
			0.42
			0.41
8	3	134.3	0.41
9	1	149.5	0.70
Hole 379A			
20	2	179.6	0.54
			0.54
20	2	179.6	0.51
			0.49
20	2	181.2	0.52
21	3	190.7	0.41
23	7	216.0	0.45
25	4	230.2	0.72
26	1	236.6	0.36
27	4	249.2	0.44
28	5	260.3	0.34
29	4	268.2	0.59
30	3	277.7	0.96
31	6	290.4	0.39
32	2	295.2	0.32
34	0	311.0	0.77
			0.75
			0.76
34	0	311.0	0.80

TABLE 2 (CONT).

Core	Section	Depth m	Org. C %
34	3	314.2	0.59
			0.45
			0.63
			0.56
			0.61
34	CC	320.5	0.50
35	4	327.6	0.28
36	5	336.3	0.65
37	2	342.7	0.37
38	7	358.5	0.32
39	4	364.8	0.38
40	5	374.3	0.25
42	4	382.2	0.58
43	4	393.3	0.25
			0.21
			0.25
			0.26
			0.24
			0.25
45	3	409.2	0.33
46	3	418.7	0.26
47	5	432.9	0.43
48	1	434.5	0.48
49	2	445.6	0.28
50	2	455.1	0.33
51	0	463.0	0.30
51	5	470.9	0.35
51	CC	472.5	0.49
52	2	474.1	0.29
53	2	485.2	0.52
54	0	491.5	0.43
54	0		0.45
			0.41
			0.41
			0.42
			0.51
54	3	496.2	0.41
55	3	505.7	0.30
56	6	520.0	0.63
57	6	529.5	0.75
58	3	532.7	0.29
59	4	543.7	0.45

TABLE 2 (CONT).

Core	Section	Depth m	Org. C %
60	5	554.8	0.33
62	3	564.7	0.25
64	4	583.3	0.34
65	3	591.2	0.52
66	3	599.2	0.41
67	1	607.1	0.47
			0.33
			0.18
			0.42
68	4	621.3	0.30
Hole 380A			
31	3	612.7	0.77
			0.58
			0.53
			0.63
			0.59
41	0	703.0	2.20
41	CC	712-5	1.71
42	0	718.5	1.32
42	CC	722.0	1.96
46	1	750.5	2.26
57	CC	864.5	3.26
63	1	912	1.80
73	4	1013	1.70
76	3	1040	1.14
78	6	1063	2.20

TABLE 3.

METHANE CONTENT IN NEARBOTTOM SECTION OF WATER COLUMN IN WESTERN BLACK SEA, After Trotsyuk et al., 1984

Measuring station	Water depth m	Depth of Sampled horizon m	Methane content x10 ml/l
543	1750	1748	61.6
544	2108	2106	885.0
545	1620	1618	147.0
546	1400	1398	227.0
547	760	758	154.0
548	70	68	27.1
549	72	70	24.2
550	70	69	3.1
551	80	79	3.1
552	94	93	4.4
553	530	529	889.0
554	20	19	1.9
555	22	21	1.9
556	25	24	1.3
557	28	27	9.9
558	33	32	2.0
559	26	25	1.2
561	44	43	5.0
562	35	34	0.5
563	40	39	0.4
564	68	67	0.6
565	85	84	1.0
566	89	88	5.8
567	90	89	7.6
568	86	85	13.4
569	114	113	7.1
570	77	76	6.7
571	1450	350	348.0
572	1760	1758	17.5
573	70	69	7.5
574	66	65	4.4
575	90	89	5.22
576	850	848	1040
577	106	105	13.4
578	91	90	9.36
579	73	72	11.0
580	193	192	74.6
581	840	838	3700
582	1370	1368	2464
583	92	91	18.0
584	2250	50	28.0
584	2250	100	14.5
584	2250	150	59.8
584	2250	175	127.9
584	2250	200	102.0

TABLE 3 (CONT).

Measuring station	Water depth m	Depth of Sampled horizon m	Methane content x10 ml/l
584	2250	250	473.2
584	2250	500	326
584	2250	1000	910
584	2250	1750	866
584	2250	1900	677.0
584	2250	1950	940.0
584	2250	2000	1088.0
584	2250	2050	1321.0
584	2250	2248	1617.0
585	1087	1085	1089
586	90	89	1.37
587	38	37	11.0
588	45	44	3.4
589	50	49	5.0
590	59	58	6.0
591	48	47	2.9
592	52	51	2.0
593	100	99	0.8
594	57	56	4.2
596	73	72	265
597	30	29	42.0
598	55	54	44.5
599	55	54	104.0
600	72	71	8.1
601	1030	1028	3422
602	800	798	2770
603	233	230	1050
604	55	54	1132
605	48	47	290
606	37	36	190
607	39	38	30.0
608	60	59	15.0
609	58	57	17.0
610	61	60	5.5
611	68	67	94
612	66	65	8.5
613	59	58	10.6
614	85	84	5.5
615	100	99	17.4
616	1600	1598	1170
617	552	550	2130
618	57	56	6.9
619	95	94	13.5
620	520	518	1900
621	632	630	1142
622	79	78	38.0
623	80	79	10.0
624	30	29	12.0
625	28	27	9.8

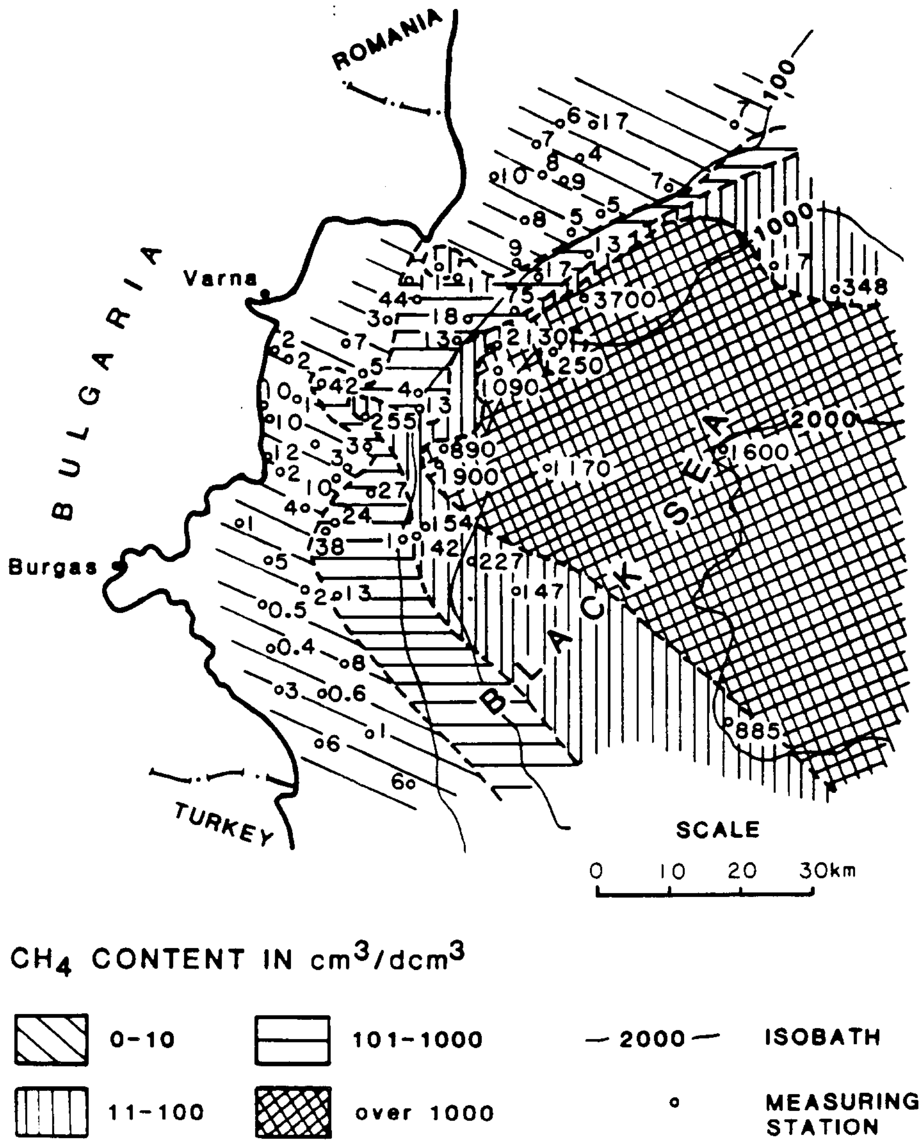


Figure 14. **METHANE CONTENT IN NEARBOTTOM WATER COLUMN OF WESTERN BLACK SEA**

After Ivanov et al., 1984

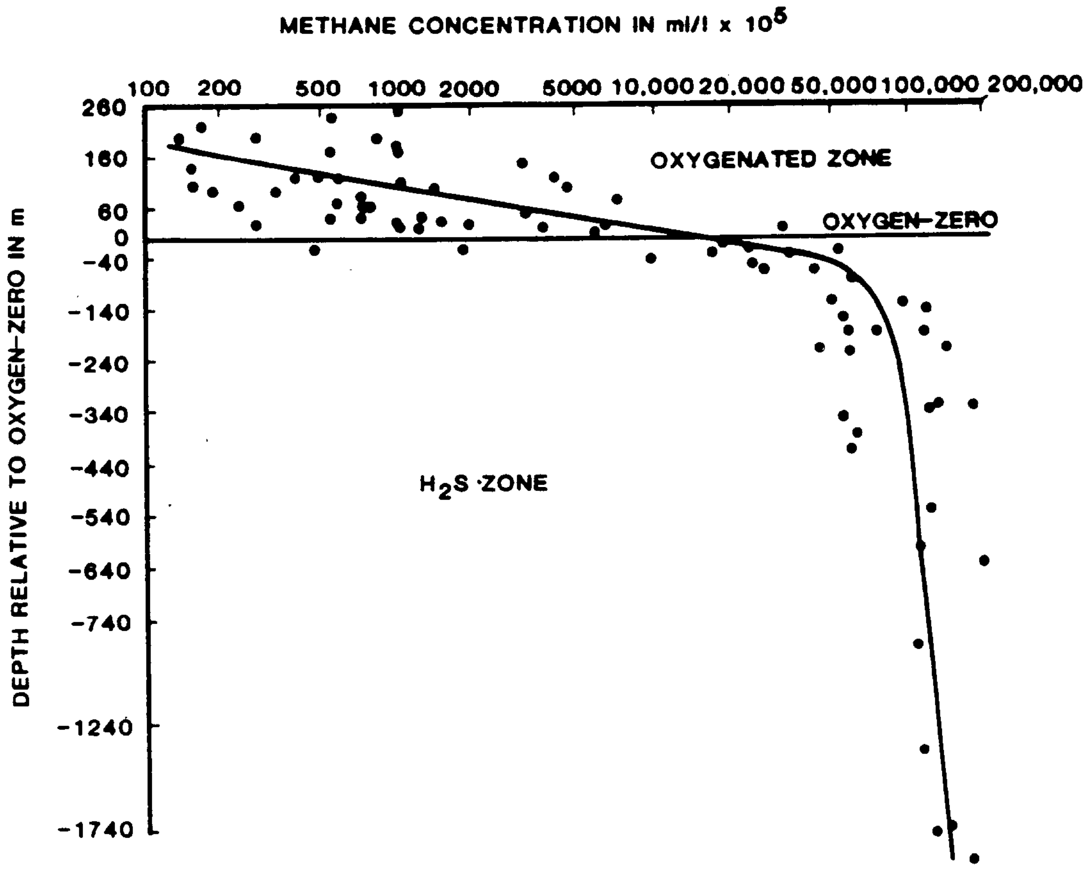


Figure 15. VERTICAL DISTRIBUTION OF METHANE IN WATER COLUMN OF BLACK SEA (based on data from 16 measuring stations)

After Hunt, 1974

$$A = a \frac{d(CH_4)}{dz} - w(CH_4)$$

where,

A = methane flux rate, in $ml/m^2/yr$
a = eddy-diffusion coefficient, in m^2/yr
w = advective velocity of CH_4 in water, in m^2/yr
$\frac{dCH_4}{dz}$ = change of CH_4 concentration of the mixing zone, ml/l

The joint amount of ethane and ethylene in the water column of the Black Sea is shown in Figures 16 and 17. Below O_2-H_2S interface, ethane represents 90% of total C_2 hydrocarbons. Therefore its changes in the H_2S zone are mainly contributing to the decreasing values of C_2+$C_{2=}$ in this zone. The oxygenated zone above the O_2-H_2S interface is known to produce olefins (e.g. ethene) while ethane as a paraffin would be actively oxidized. In view of these processes, the decrease of C_2+$C_{2=}$ in the aerobic zone is a joint result of the amount of C_2 entering the zone, oxygenation processes and $C_{2=}$ generation rate. The actual boundary of the zone with increased olefin production can be easily delineated on the graph $C_2/C_{2=}$ versus depth (Figure 3). The graph also illustrates well the hydrocarbon preservation in the H_2S zone of the water column.

Vertical and horizontal distribution of hydrocarbons, and their contents in waters of the Black Sea can be mostly explained by the biogenic generation of these gases in shallow subbottom sediments. The distribution of hydrocarbons is certainly controlled to a much lesser degree by their generation in the water column.

Hydrocarbons in Sediments

Hydrocarbon gases at shallow subbottom depths were commonly detected by Russians during early investigations of nearbottom sediments in the Black Sea in the 1960s. Some data on hydrocarbon gas content in the sediments to the maximum depth of 4.2 m are shown in Table 4. These results were obtained with utilization of hermetic core barrels and vacuum-mechanical degassing of sediment samples. The practice of collecting the water and sediment samples at the same locations made it possible to extend the analyses from water to the sediment column. Comparing values of hydrocarbons in Tables 4 and 5, it is readily noticeable that concentrations of methane in nearbottom sediment are usually several orders of magnitude higher than in the respective water column. Although increased content values of higher homologues of CH_4 were detected in the sediments, their total amount rarely exceeded 1%. Despite the low efficiency of the core barrel used, which apparently influenced the results, the fact remains that CH_4 concentrations within 3 m of sediments showed dramatic increases downward at many sampling stations.

Some other data on gas content in sediments collected with a piston-core devise from the shallow subbottom depths of the Black Sea during the Atlantis II expedition were published by Hunt (1974). The author reported that:

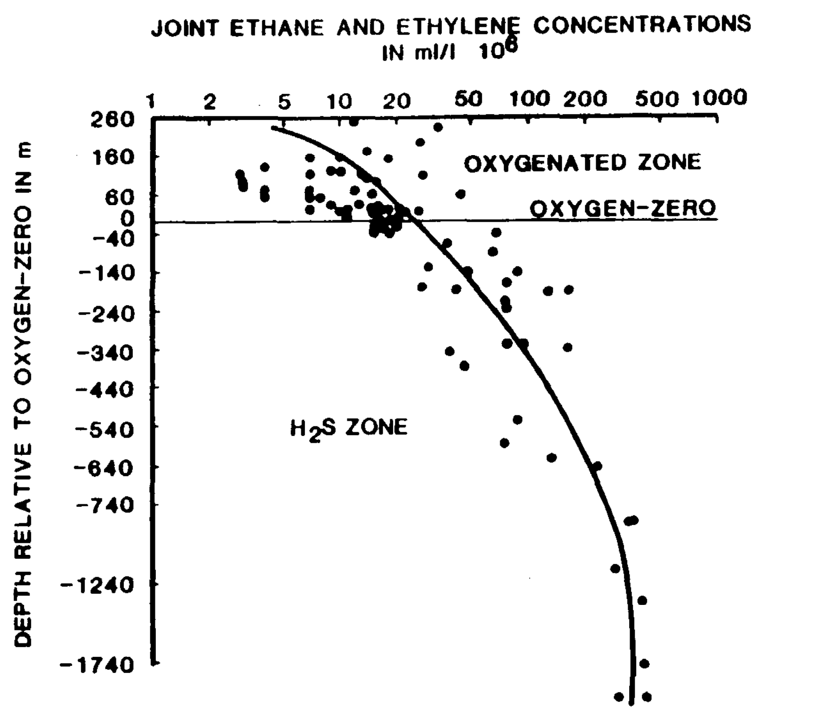


Figure 16. VERTICAL DISTRIBUTION OF ETHANE AND ETHYLENE IN WATER COLUMN OF THE BLACK SEA
(based on data from 6 measuring stations)

After Hunt, 1974

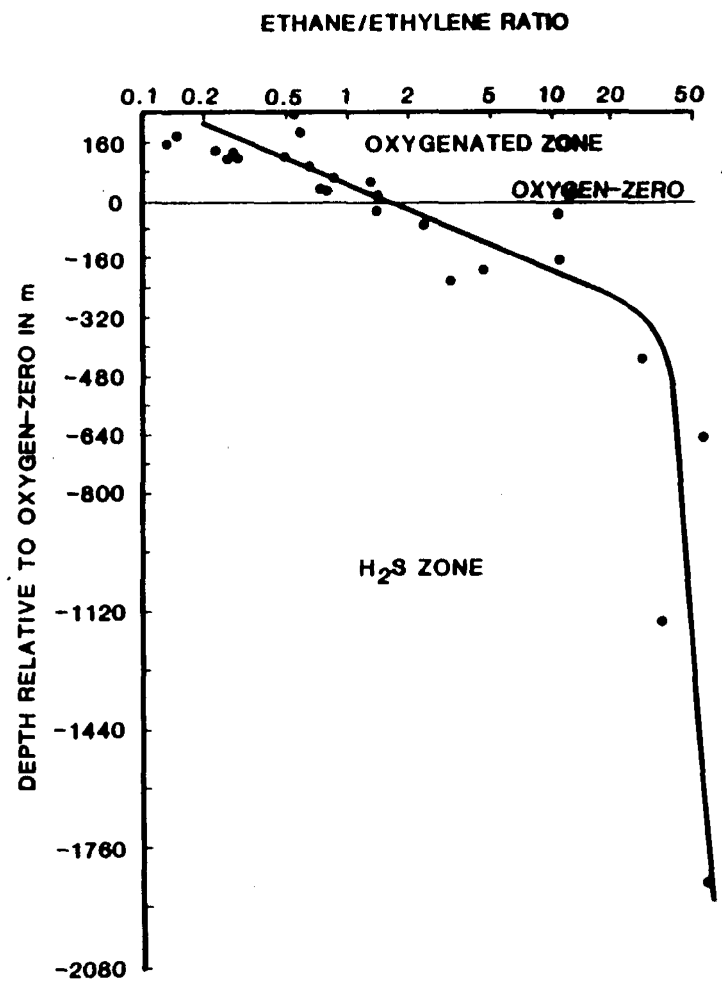


Figure 17. ETHANE/ETHYLENE RATIO IN VERTICAL PROFILE OF WATER COLUMN IN THE BLACK SEA

After Hunt, 1974

TABLE 4.

CONTENTS OF HYDROCARBON GASES IN BOTTOM SEDIMENTS IN WESTERN BLACK SEA, After Bolshakov et al., 1984

Station No.	Water Depth m	Subbottom Depth of Sampled Horizon m	Hydrocarbon Gases Content x 10^{-4} ml/kg of sediment				
			CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6
543	1750	30-35	52.4			10.5	0.5
		55-60	1786			0.1	0.4
		160-165	600				
		320-330	60368			0.1	
544	2108	100-110	1265				
		250-260	1850				
		310-320	4250				
545	1620	260-270	121				
546	1400	90-100	60.9	0.6	1.2	0.4	0.8
		160-170	61.6	0.7	1.7	0.2	0.5
548	70	70-80	29.2				
551	80	60-80	71.8	0.1	0.2	0.3	
		100-120	72.0				
		140-160	178	0.1	0.4		
		180-200	1594				
		60-80	255				
		140-160	129				
554	21	20-30	2.5				
555	22	20-30	2.9	0.1	0.3	0.1	
		150-160	16632				
		300-310	32571				12.9
556	25	20-30	6.3				4.5
558	33	30-40	330.3				4.5
559	26	30-40	343.0	1.1		0.1	0.4
		320-330	4805	0.1	0.2	0.8	1.4
		200-210	52.4	7.6	9.1	3.8	5.7
		80-100	3272				
560	25	100-110	881	24.5	33.0	19.5	42.8
		30-40	14784				
563	40	30-40	624	11.6	23.0	3.0	9.8
564	68	30-40	692			0.6	2.8
		140-160	96600				
		140-150	44400				
		240-250	142300				
565	85	20-30	2250				
566	89	20-30	9009				
567	90	20-30	1663				
568	86	50-60	185				
		140-160	828				
		130-140	475				

TABLE 4 (CONT).

Station No.	Water Depth m	Subbottom Depth of Sampled Horizon m	Hydrocarbon Gases Content x 10^{-4} ml/kg of sediment				
			CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6
		230-240	308				
569	114	20-30	226	0.5	1.3		
570	77	20-30	66.6	0.9	2.8	0.3	1.3
571	1450	20-30	80.0				
	1475	70-80	13800				
		180-200	47432			3.0	2.2
		300-320	66530				
572	1760	30-40	186			0.5	1.5
573	70	30-40	376	3.0	9.7	0.1	0.3
575	90	30-40	182.4	1.1	1.0	0.1	0.4
576	850	40-60	8316	0.9	0.2		
		40-60	1775				
		80-90	1572				
		200-210	101640				
		300-340	115546				
577	106	30-40	11550				
578	91	30-40	2900				
579	73	30-40	52.0				
580	193	20-30	624				
		110-120	13475				
		210-220	231000				
581	860	40-50	2884				
582	1370	140-160	505.7				
		180-190	20100				
		140-160	15015				
		200-210	86400				
583	92	20-30	114	0.6	1.2		
584	2200	60-80	186	2.1	1.2		
		90-100	128				
		200-220	16817				
585	1087	30-40	501				
586	90	20-30	46.8				
		60-70	4.5				
587	38	20-30	8.0				
588	45	30-40	66.7				
590	59	30-40	2400				
		90-100	176730				
		100-120	351450				
		100-110	53900				

TABLE 4 (CONT).

Station No.	Water Depth m	Subbottom Depth of Sampled Horizon m	Hydrocarbon Gases Content x 10^{-4} ml/kg of sediment				
			CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6
		190-200	191000				
		300-310	93100				
591	48	10-20	403				
592	52	20-30	6120				
593	100	100-110	756				
594	57	20-30	730				
		210-220	161700				
		300-310	254100				
		400-410	28880				
593	45	20-30	12000				
		210-220	119000				
		320-330	97800				
596	73	20-30	3270				
		100-110	2750				
		210-220	44350				
		300-310	143900				
		380-390	27630				
598	55	30-40	3288				
		100-110	7161				
		190-200	53657				
		310-320	127050				
		380-390	72973				
599	55	20-30	576				
600	72	30-40	2500				
601	1065	30-40	160				
		140-160	109340				
		250-260	250000				
		380-390	4435				
602	800	20-30	1800				
603	233	20-30	1435				
		100-110	196000				
		200-210	152000	--	--	1.1	1.2
		300-310	40650				

When the plastic liners were removed from the barrels at some stations, the mud column began to expand as a result of the formation of gas pockets within the core.

The results of geochemical-isotopic analyses of gas recovered from core 1846K of an unspecified location at the Black Sea are shown in Table 5.

TABLE 5.

ANALYSES OF GASES FROM THE BLACK SEA CORE 1486K
After Hunt, 1974

Subbottom Depth cm	Component Height %				Unknown***	Carbon Isotopic Composition $\delta^{13}C$ (PDB Standard)	
	CO_2	H_2	N_2	CH_4		$\delta^{13}C(CH_4)$	$^{13}C(CO_2)$
435	.53	.05	6.70	91.79	.93	-68.3	Y**
640	.32	.27	11.41	88.00	X	-69.6	Y
720	.98	X*	5.70	92.59	.72	-68.4	Y
800	2.07	.10	6.31	91.52	X	-67.6	Y

* Not detected
** Insufficient samples available for isotopic analysis
*** Unknown substance was eluted from chromatogram after n-penthane. Probably it was not hydrocarbon.

As in the Russian analyses, methane appears to be a major gas element and the only hydrocarbon detected. Apparently its percentage remains fairly constant and high (>90% of total gas) throughout the entire analyzed interval. This indicates that a substantial portion of this gas had been generated biogenically from in situ sediment. The presence of molecular hydrogen with carbon dioxide is acceptable based on the provision that both elements are essential in microbial metabolic processes during biogenic methanogenesis. The carbon isotopic values of methane vary within a range commonly referred to microbially produced CH_4.

Although the analyses of gases in the Black Sea sediments did not involve precise quantitative measurements, it had been estimated that 500 cm of sediment yielded approximately 30 cm of gas at STP. Based on the assumption that most of the sediment gas in the Black Sea is originated in 1 m of the sea floor mud over the deep water area of approximately 100,000 km^2, 6 x 10^{11} L of CH_4 should be present in this zone.

Expanding gases had been frequently noted from cores recovered at DSDP sites 379, 380, and 381 in the Black Sea (Hunt et al., 1978; McIver, 1978). Again, as will be shown in the following chapters, geochemical characteristics strongly confirm the biogenic provenance of these hydrocarbons.

Biogenic Methanogenesis

The processes of biogenic methanogenesis have been described in detail in numerous professional papers (e.g. Claypool and Kaplan, 1974; Cherskii and Tsarev, 1977; Rice and Claypool, 1981). Therefore, only a short recapitulation of the major stages of these processes will be presented in conjunction with relevant geochemical findings in Black Sea sediments and pore fluids.

Biogenic methane has been found to be one of the end products of the anaerobic bacterial decomposition of organic matter which may start at temperatures well below 50°C. The methane-producing bacteria are strictly anaerobic and cease to grow with the presence of oxygen, even in trace amounts. Another characteristic of the CH_4-producing bacteria is their lack of growth in the presence of sulfate. Such requirements strictly delineate the environments in which biogenic methanogenesis can occur. Generally two groups of metabolic reactions producing acceptors for electrons generated in degradation of organic matter take place during these processes. The first group of the reactions is often referred to as respiratory reactions which occur in aerobic and anaerobic conditions as well. The anaerobic respiratory reactions include:

a. nitrate reduction

$$5CH_2O + 4NO_3^- + 4H^+ \longrightarrow 2N_2 + 5CO_2 + 7H_2O$$

b. sulfate reduction

$$2CH_2O + SO_4^{2-} \longrightarrow S^{2-} + 2CO_2 + 2H_2O$$

c. carbonate reduction

$$4H_2 + HCO_3^- + H^+ \longrightarrow CH_4 + 3H_2O$$

d. nitrogen fixation

$$3CH_2O + 2N_2 + 3H_2O \longrightarrow 4NH_3 + 3CO_2$$

The second group of known reactions in biogenic methanogenesis is the formation of glucose and amino acids. Formation reactions are energetically inferior to the respiratory processes which probably determines their smaller role in direct production of methane. The greater importance of fermentation processes is seen in the chain of reactions which lead to breaking the organic structures of sugars and amino acids. In this way the latter processes can be viewed as preparatory steps for the respiratory processes. A precisely defined sequence of geochemical environments usually results when these processes occur (Figure 18). When oxygen is depleted, the aerobic bacteria are substituted by sulfate-reducing bacteria which delineate the upper area of anaerobic conditions. The characteristic chemical elements of the latter area are such ions as: SO_4^{2-}, HS^-, HCO_3^-. The sulfate-reducing zone features gradual depletion of sulfates dissolved in interstitial water, but increased values of S^{34} can be observed. Ultimately the sulfate-reducing zone is substituted by the carbonate or carbon dioxide reducing zone. Reduction of carbon dioxide appears to be a dominant process of anaerobic respiration resulting in formation of methane. The availability of hydrogen for these processes, however critical, is still not adequately known. Claypool and Kaplan (1974) invoked two types of hydrogen producers:

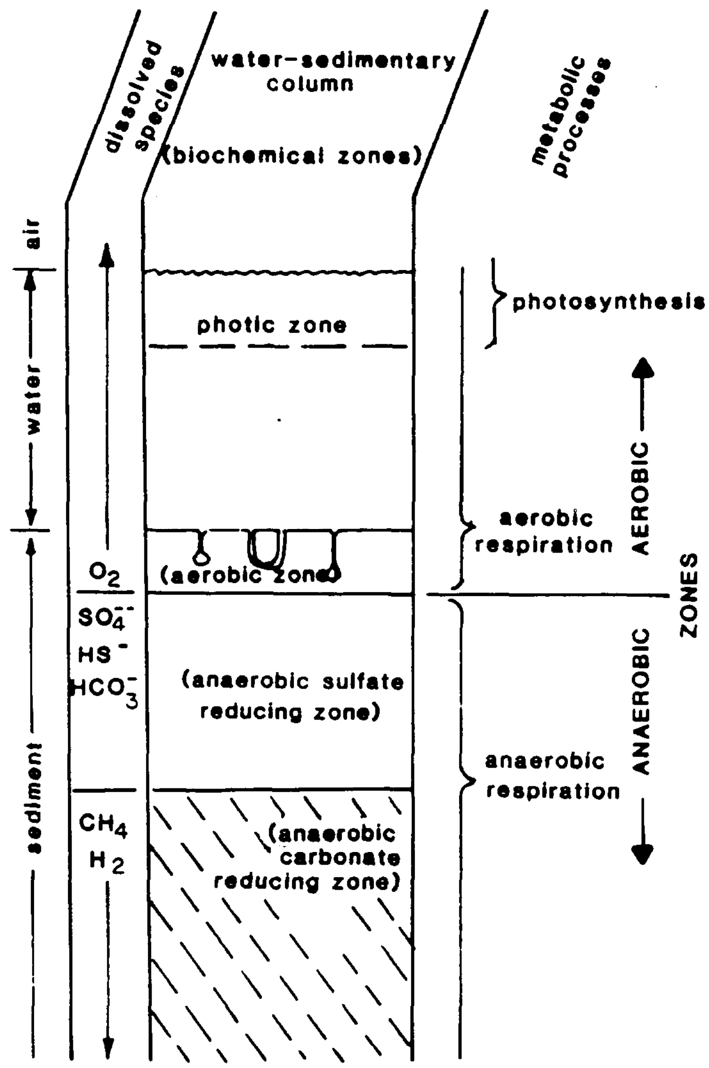


Figure 18. SUCCESSION OF MICROBIAL ECOSYSTEMS LEADING TO BIOGENIC METHANE GENERET GENERATION

After Claypool and Kaplan, 1974

1. Microorganisms yielding H^+ according to the reaction shown below while symbiotic methane producers are present.

$$CH_3CH_2OH + H_2O \longrightarrow CH_3COOH + H_2O + H_2$$

2. Variety of fermenting bacteria can produce hydrogen instead of degraded organic chains in presence of hydrogen-consuming organisms.

As the reduction of sulfates and methanogenesis are mutually exclusive in marine sediments (Claypool and Kaplan, 1974; Kosiur and Warford, 1979), the second process does not take place where sulfates are present. The organic matter which is preserved in the sulfate zone is subjected to degradation processes which are accelerated by the removal of H_2. The rate of this removal depends on the availability of carbon dioxide.

The isotopic indicators are often used in deciphering hydrocarbon origin. The biogenic methanogenesis is usually well reflected in isotopic values of such geochemical elements as $\delta^{32}S$, $\delta^{34}S$, $\delta^{13}C_{methane}$ and $\delta^{13}C_{CO_2}$. These isotopes provide important information with regard to the above described environments where the biogenic hydrocarbons are generated. The effects of bacterial sulfate reduction and dissolved sulfate depletion with depth are recorded in the changing values of the isotopes $\delta^{32}S$ and $\delta^{34}S$. As a result of preferential $\delta^{32}S$ removal, the pore water is relatively enriched in $\delta^{34}S$. The carbon isotopic composition of carbon dioxide and methane are commonly characterized by the isotopic factor $\delta^{13}C$ which is defined as (values are reported in "per mil"):

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C) \text{ sample}}{(^{13}C/^{12}C) \text{ PDB standard}} - 1 \right) \times 1000$$

The interpretation of $\delta^{13}C_{CO_2}$ is more complex than with sulfate due to fluctuations of carbon dioxide dissolved in pore water, related to methane formation. The onset of methane formation is characterized by a relatively high concentration of carbon dioxide (approximately .022 M) and $\delta^{13}C_{CO_2}$ of -22 per mil as a result of total depletion of sulfate and input of metabolic carbon dioxide in the interstitial water. Subsequent removal of isotopically light carbon dioxide in the process of methane formation causes a decrease of carbon dioxide concentration and an increase of $\delta^{13}C$ of the residual $\delta^{13}C$. The most apparent result of such interactive processes is the parallel relationship between the concentration of isotopic values of carbon in carbon dioxide and CH_4 in biogenic methane producing environments. The values of $\delta^{13}C$ of biogenic methane commonly are below the range of -55 to -60 per mil.

Geochemical zones required for the biomethanogenesis to occur can be easily recognized in the Black Sea basin. In the water column, the topmost oxidized zone is 100 to 150 m thick (Figure 10) where oxygen content varies from 6.5 ml/l to the analytic zero at the lower boundary. Hydrogen sulfate in the Black Sea is usually detected at a water depth of 125 m. Its content increases dramatically with depth from 0 to 6.5 ml/l at 1,000 m. In a nearbottom section of the water column, H_2S content exceeds 7.8 ml/l. According to geochemical data published by Ivanov et al. (1984) from the area

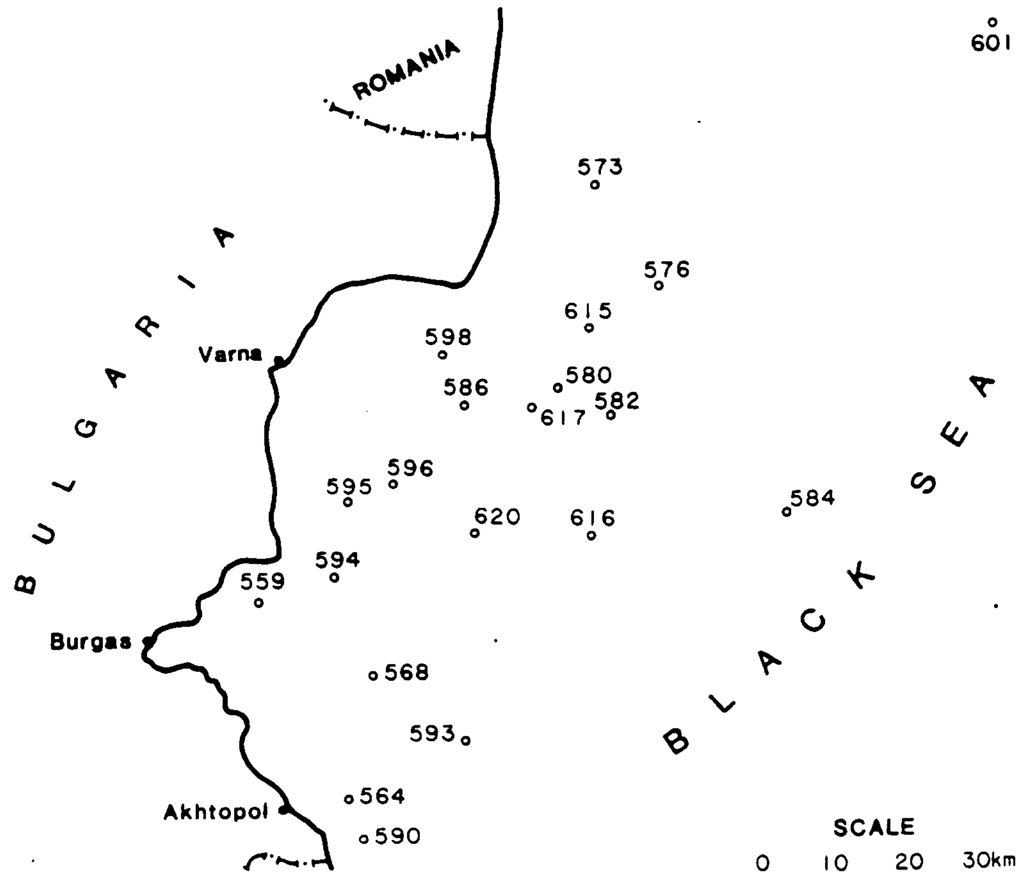


Figure 19. LOCATION OF SOME MEASURING STATIONS IN THE BLACK SEA

TABLE 6.

INTENSITY OF SULFATE REDUCTION IN NEARBOTTOM SEDIMENTS OF WESTERN BLACK SEA, After Ivanov et al., 1984

Station	Sea depth m	Subbottom depth of sampled interval cm	Dissolved SO_4^{2-}, S mg per 1 kg of sediment
601	1065	0-2	378
		2-5	242
		10-15	211
		30-50	6
		100-125	75
582	1370	5-10	344
		10-15	416
		50-70	338
		160-180	266
		210-230	194
571	1450	2-5	298
		10-15	314
		25-40	251
		80-100	202
545	1620	0-30	372
		30-60	294
		80-100	254
		110-140	72
384	90	2-5	344
		10-15	550
		50-70	334
		70-90	122
		100-120	97
559	26	5-10	232
		40-60	159
		250-270	115
		320-350	26
555	22	2-5	172
		7-10	163
		40-60	125
		80-100	103
		135-160	42

TABLE 6 (CONT).

Station	Sea depth m	Subbottom depth of sampled interval cm	Dissolved SO_4^{2-}, S mg per 1 kg of sediment
598	55	0-1	438
		2-5	151
		5-10	202
		50-70	104
		200-220	37
590	59	0-1	438
		2-5	151
		10-15	148
		160-180	49
568	55	0-2	440
		5-10	201
		20-40	273
		90-110	190
		210-230	155
580	193	5-10	335
		15-20	267
		60-80	113
		150-170	138
		200-220	55
		290-310	53

of the western Black Sea (Table 6), the indications of sulfate reduction processes were observed in all bottom sea sediments. The most progressive sulfate reducing apparently takes place in upper horizons of the investigated intervals. At the same time the intensity of these processes decreases with depth. Some analytical results of isotopic values of ^{34}S of sulfate from the Black Sea stations conform well with values characteristic of anoxic environments. In all stations shown, enrichment in heavier isotope ^{34}S in pore water with depth is readily noticeable. The ^{34}S values of sulfate ions in pore water from shallow sedimentary horizons in shelf areas range from +18 per mil (station 573) to +20 per mil (station 590), and in bathymetrically deeper locations the comparable ^{34}S values range from +20 per mil to +20.6 per mil (station 590). These values show that indeed there is not much variation of ^{34}S in bottom and nearbottom sediments in various bathymetric locations of the Black Sea. Instead, a significant increase of heavier isotope ^{34}S content had been measured at deeper intervals within the sedimentary column where in some stations (e.g. 559) ^{34}S exceeded 29 per mil. The Russian isotopic data from some stations also revealed significantly higher concentrations of the heavy isotope ^{34}S in shallow water areas of the Black Sea compared to the locations with thicker water columns. This was mistakenly interpreted as low intensity reducing processes in shelf areas (Migdisov et al., 1974). The newer data showed that the maximum of sulfate generation processes occurs in the shallow water reducing zone in clayey sediments. Subsequently it was concluded that in shelf areas the biogenic reducing conditions are much less likely to occur than in deep water zones (Migdisov et al., 1974; Ivanov et al., 1984).

The intensity of methane generation in nearbottom sediments (0 to 350 cm) of the western Black Sea are shown in Table 7. The data indicate that bacterial methane generation occurs presently within all sediments investigated to a subbottom depth of 350 cm. The investigated methane generated at a rate of .46 x 10^{-6} cm^3 per 1 kg of sediment per day appears to be mostly a product of carbon dioxide reduction. The maximum values of carbon dioxide reduction and CH_4 generation were detected in sediments enriched in organic matter (>1% organic matter), of middle Holocene age. The lowest rates of methane generation from carbon dioxide reduction were found in coccolith muds of lower Holocene where depletion in organic matter was noted (stations 545 and 584). The magnitude of methane-generating processes showed a strong relationship with the bathymetry of the Black Sea. The increase of this magnitude was observed from the shelf to the lower continental slope. This trend correlates well with increasing values of organic carbon in sediments. Opposite trends have been found with respect to acetate fermentation processes which decrease with distance from the sea shores (Table 8). Subsequently the role of methane generated from acetate is significantly diminished in deeper parts of the Black Sea basin. The isotopic concentration factors ^{13}C of methane were analyzed at stations 545 and 590 on gas samples collected from the subbottom depths of 140-160 and 100-120 cm respectively. In both cases, the isotopic values (-78.4 and -81.8 per mil) conform with the standards assigned to biogenically derived methane (Fuex, 1977; Schoell, 1983; Waples, 1981).

TABLE 7.

METHANE CONTENT IN BLACK SEA BOTTOM SEDIMENTS, After Ivanov et al., 1984

Station	Sea depth m	Subbottom depth of gas sample, cm	CH_4 content 10^{-4} cm^3 per 1 kilogram of clayey sediment	Age of sediments, years	Rate of CH_4 generation 10^{-6} cm^3/kg/day	Calculated content of CH_4 in cm^3 per 1 kg of sediment	Percentage of CH_4 retained in sediments,
555	22	150-160	1.66	1973	19.1	13.69	12.1
559	26	30-40	0.034	491	8.5	1.54	2.2
		320-330	0.47	3283	14.5	17.42	2.7
568	55	50-60	0.019	795	8.6	2.49	0.7
		230-240	0.03	7635	7.6	21.4	0.1
580	193	20-30	0.06	398	2.1	0.3	21.0
		210-220	23.2	4830	71.6	125.8	18.4
617	1600	20-30	0.01	398	2.1	0.3	3.5
		240-250	15.40	7000	17.6	44.7	26.3
582	1370	20-30	0.008	3450	43.7	57.0	0.012
		160-180	1.75	22019	14.5	118.3	1.4
		200-210	8.64	28082	39.1	397.2	2.1
616	1600	35-60	0.17	3855	220.0	397.2	2.1
		100-110	0.015	8080	1.2	3.08	0.5
584	2200	60-80	0.019	6461	7.96	18.71	0.1
		90-100	0.013	7604	8.8	24.3	0.05

TABLE 8.

METHANE GENERATION IN THE REDUCING PROCESS OF HCO AND ACETATE IN PLEISTOCENE AND HOLOCENE SEDIMENTS OF WESTERN BLACK SEA, After Ivanov, 1984

Station	Sea depth m	Sampled interval cm	Organic carbon content %	HCO_3^- content mg per 1 kg of sediment	Acetate content mg per 1 kg of sediment	Rate of CH_4 generation 10^{-6} cm per 1 kg of sediment			Percentage of CH_4 generated from acetate
						from HCO_3^-	from acetate	total	
555	22	7-10	0.3	70.5	1.3	12.5	0.19	12.7	1.5
		40-60	0.3	74.4	0.69	15.3	0.36	15.7	2.3
		80-100	0.6	81.8	0.51	5.6	0.26	5.9	4.4
		135-160	0.36	251.8	0.83	18.9	0.24	19.1	1.3
559	26	5-10	0.47	89.5	0.84	4.5	0.13	4.6	2.8
		40-60	0.3	108.3	2.04	8.2	0.31	8.5	3.7
		250-270	0.24	172.2	0.25	16.1	0.04	16.1	0.25
		320-350	0.12	183.4	0.96	14.4	0.13	14.5	0.9
568	55	5-10	0.54	137.9	0.0	26.6	0.0	26.6	0.9
		20-40	0.73	161.7	0.41	8.4	0.16	8.6	1.9
		90-110	0.19	273.9	---	26.2	---	---	---
		210-230	2.08	360.8	1.1	7.5	0.1	7.6	1.3
580	193	5-10	0.67	318.4	0.19	2.1	0.04	2.1	1.9
		15-20	0.58	314.8	0.33	2.1	0.04	2.1	1.9
		60-80	1.2	689.8	0.71	73.1	0.28	73.4	0.38
		150-170	1.87	859.1	0.89	66.2	0.63	66.8	0.94
		200-220	1.56	902.3	2.44	71.1	0.54	71.6	0.74
		290-310	1.93	674.7	0.92	17.4	0.19	17.6	1.08

TABLE 8 (CONT).

METHANE GENERATION IN THE REDUCING PROCESS OF HCO AND ACETATE IN PLEISTOCENE AND HOLOCENE SEDIMENTS OF WESTERN BLACK SEA, After Ivanov, 1984

Station	Sea depth m	Sampled interval cm	Organic carbon content %	HCO_3^- content mg per 1 kg of sediment	Acetate content mg per 1 kg of sediment	Rate of CH_4 generation 10^{-6} cm^3 per 1 kg of sediment			Percentage of CH_4 generated from acetate
						from HCO_3^-	from acetate	total	
582	1370	5-10	1.43	281.2	0.96	44.7	0.66	45.4	1.5
		50-70	0.47	218.6	2.68	57.8	0.53	58.0	0.9
		160-180	0.36	160.0	0.85	14.4	0.30	14.7	2.04
		210-230	0.22	141.3	1.06	38.9	0.05	39.0	0.12
543	1600	0-30	1.37	261.3	5.9	0.46	1.6	2.06	77.60
		30-60	2.7	456.8	0.9	220.0	0.32	220.3	1.04
		80-100	3.4	482.6	2.58	213.0	2.23	215.2	1.04
		110-140	0.6	427.3	2.55	less than 0.74	1.05	---	---
584	2200	5-10	1.95	211.5	0.39	less than 0.37	0.08	---	---
		10-15	1.65	233.6	1.09	less than 0.4	0.54	---	---
		50-70	2.5	306.4	4.17	5.6	2.36	7.96	30.0
		70-90	0.26	134.8	2.7	6.9	1.91	8.8	21.7
		100-120	0.34	178.5	---	3.6	---	---	---

Geochemical characteristics of gases in deeper sediments of Black Sea basins were obtained from the analyses of gas samples recovered from the cores at the DSDP Sites 379, 380 and 381 (Tables 9 and 10; Figures 20 and 21). These data confirm the previously made contention about the biogenic origin of hydrocarbon gas. Methane is a major component constituting over 98% of total hydrocarbons. The concentrations of CH_4 and carbon dioxide show decreasing trends with increasing depth (Figure 20). Although these trends are occasionally masked by high carbon dioxide concentrations, the parallel relationship between the two components is noticeable in all three profiles.

The isotopic values of $\delta^{13}C$ obtained from the methane fraction of the sampled gas, range from -70 per mil to -55 per mil (PDB). Such values showing a slight enrichment with depth are typical for immature gases. It must be noted, however, that some extreme values of $\delta^{13}C$ were measured at sites 379 (-34.2 per mil at 33 m depth and -48.4 per mil at 52.5 m depth) and 381 (-37.5 per mil at 133 m depth; Table 10). The latter $\delta^{13}C$ values can be explained within boundaries of biogenic hydrocarbon generation. One explanation was offered by Lebedev et al. (1969) who contented that heavy $\delta^{13}C$ values may be caused by the bacterial oxidation of methane during a sea level regression. In such a situation, bacteria preferentially oxidize light methane leaving relatively heavier elements. According to Galimov (1967), Columbo et al. (1969), and Lebedev and Lyngayevski (1971), hydrocarbon migration may lead to carbon isotope fractionation, resulting in enrichment or depletion of methane with the isotope $\delta^{13}C$. The latter contention, although based on laboratory experiments, faced the opposing views expressed by Bernard et al. (1977) and Stahl et al. (1974). These authors conceded that no consistent and significant $\delta^{13}C$ isotope effects caused by migration have been observed under natural conditions.

The higher hydrocarbon gases (i.e. to pentanes) were detected in small quantities at all three Black Sea DSDP locations (Table 9). At Site 381, the concentrations of these components increase to a depth of approximately 350 m where a break toward lower values can be observed. The comparison of the ratio between branched and straight hydrocarbon chains is often used in analyses of their source. Ratios of isobutane:n-butane in profiles of the holes 379A and 381, with minor exceptions, do not show any major changes. Conversely the ratios of isopentanes:n-pentanes in all three profiles exhibit a general trend of increase with depth (Figure 21). Such trends are explained by the presence of increased amounts of isopentane whereas n-pentane appears to be constant with depth (Hunt and Whelan, 1978). Investigations of the relationship between the temperature and content of isopentanes and n-pentanes for the Paris Basin showed significant stability of n-pentane and shrinking amounts of isopentane with depth. At the same time more isopentane is available during early biogenic and diagenetic reactions of organic matter. Considering additionally the fact that Davis and Squires (1954) and Kim and Douglas (1972) demonstrated that trace amounts of higher alkanes (ethane-propane) could be experimentally generated through fermentation, it is safe to conclude that presence of hydrocarbons as high as propanes does not preclude their biogenic origin.

All data presented above strongly suggests that at least a predominant portion of hydrocarbon gases in the Black Sea water column and 1,000 m-thick sediment column has been formed in situ through biogenic processes, not as a result of thermogenic gas diffusion from a sedimentary pile at greater depth.

TABLE 9.

HYDROCARBON COMPOSITION OF GASES FROM CORES AT DSDP SITES IN BLACK SEA, After Faber et al., 1978

Depth (m)	Percentage of Gas Components							$\frac{i\text{-}C_4H_{10}}{n\text{-}C_4H_{10}}$	$\frac{i\text{-}C_5H_{12}}{n\text{-}C_5H_{12}}$
	CH_4	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$i\text{-}C_5H_{12}$	$n\text{-}C_5H_{12}$		
					Hole 379B				
54.50	99.53	0.20	0.12	0.06	0.09	---	---	---	---
83.00	99.96	0.01	0.01	0.00	0.01	0.01	---	---	---
140.00	98.84	0.01	0.02	0.01	0.02	0.95	0.15	0.50	6.34
					Hole 380A				
376.50	99.81	0.06	0.03	0.01	0.01	0.03	0.05	2.50	0.58
427.50	99.95	0.03	0.01	0.01	0.01	---	---	---	---
525.50	99.84	0.13	0.01	0.02	---	---	---	---	---
1038.50	98.55	0.68	0.36	0.12	0.03	0.27	---	---	---
1062.00	95.84	1.14	1.44	0.77	0.21	0.60	---	---	---
					Hole 380				
0.00	99.98	0.00	0.00	0.00	0.01	0.00	0.00	0.33	---
4.50	99.99	0.00	0.00	0.00	---	---	0.00	---	---
6.00	99.91	0.01	0.00	0.04	0.03	0.00	---	---	---
90.00	99.93	0.02	0.01	0.00	0.00	0.02	0.00	0.67	14.00
171.00	99.54	0.01	0.03	0.10	0.07	0.16	0.10	1.50	1.67
199.50	99.91	0.01	0.01	0.01	0.00	0.02	0.04	1.50	0.67
209.00	99.98	0.01	0.01	0.01	0.00	0.00	---	---	---
217.00	99.98	0.00	0.01	0.00	0.00	0.00	0.00	2.00	1.00
228.00	99.95	0.01	0.01	0.01	0.01	0.01	0.01	0.50	1.00
					Site 381				
3.75	99.99	0.01	---	---	---	---	---	---	---
6.00	99.98	0.02	---	---	---	---	---	---	---
95.00	99.99	0.01	---	---	---	---	---	---	---
104.50	99.97	0.02	0.00	0.01	---	---	---	---	---
133.00	100.00	0.00	---	---	---	---	---	---	---
335.50	99.63	0.32	0.06	---	---	---	---	---	---

TABLE 10.
COMPOSITION AND ISOTOPIC RATIOS OF GASES FROM DSDP SITES OF LEG 42, BLACK SEA, After Faber et al., 1978

Subbottom depth m	Gas Content in vol %			$\frac{CO_2}{CH_4}$	$\delta^{13}C_{CH_4}$	$\delta^{13}C_{CO_2}$
	Air	CH_4	CO_2			
Site 379						
1.50	83.22	14.84	1.94	0.13	-63.8	----
33.00	95.49	2.28	2.24	0.98	-34.2	----
52.50	92.93	3.19	3.88	1.22	-48.4	----
71.50	81.89	11.76	6.35	0.54	-60.0	----
89.00	91.79	5.29	2.92	0.55	-58.1	----
117.50	90.12	7.82	2.06	0.26	-57.7	-4.9
130.50	89.74	8.97	1.28	0.14	-60.8	-3.0
136.50	97.69	1.76	0.55	0.31	-48.0	----
216.00	89.07	8.32	2.61	0.31	-64.5	-3.1
301.50	88.58	10.11	1.31	0.13	-60.5	----
320.50	97.40	1.47	1.13	0.77	-58.8	-8.2
49.50	93.26	4.13	2.62	0.63	-50.4	----
330.00	96.61	2.71	0.68	0.25	-61.1	-8.6
349.00	98.98	0.52	0.49	0.94	-55.5	-7.7
380.00	98.97	0.94	0.09	0.10	-53.4	----
396.50	96.54	3.19	0.26	0.08	-55.7	----
434.50	94.30	5.55	0.14	0.03	-63.3	----
439.00	95.64	3.26	1.10	0.34	-55.1	-6.8
453.50	96.99	2.68	0.32	0.12	-59.1	----
472.50	92.22	6.97	0.81	0.12	-61.3	-9.5
520.00	96.65	3.22	0.13	0.04	-59.7	----
Site 380B						
0.00	91.62	8.38	----	----	-80.4	----
4.50	92.21	7.79	----	----	-71.3	----
6.00	95.47	4.53	----	----	-43.0	----
90.00	93.86	6.13	----	----	-58.0	----
171.00	96.85	3.13	----	----	----	----
199.50	95.75	4.25	----	----	-61.0	----
209.00	88.25	11.74	----	----	-63.2	----
217.00	91.01	8.99	----	----	-60.5	----
228.00	96.16	3.84	----	----	-60.8	----
Site 381						
3.75	94.55	4.73	0.73	0.15	-74.6	-18.6
6.00	98.29	1.30	0.41	0.32	-72.2	-23.7
95.00	88.15	11.53	0.32	0.03	-64.5	-29.9
104.50	91.40	7.87	0.44	0.06	-64.3	-20.0
133.00	97.33	2.39	0.28	0.12	-37.5	-14.7
335.50	97.93	1.79	0.27	0.15	-65.7	-11.5

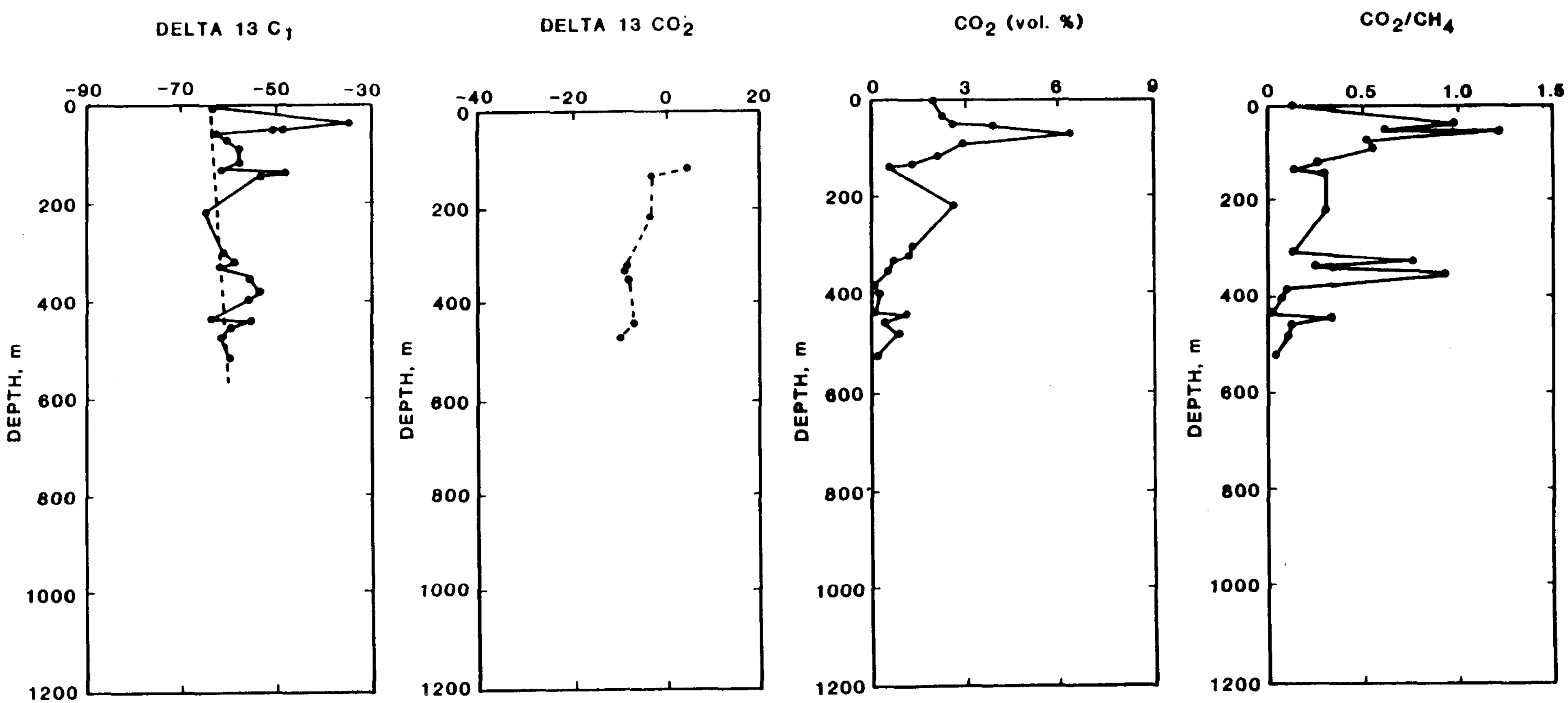


Figure 20. RESULTS OF CHEMICAL AND ISOTOPIC (% PDB) ANALYSES OF CH_4 AND CO_2 IN SEDIMENTS OF THE BLACK SEA AT DSDP SITE 379

After Faber et al., 1978

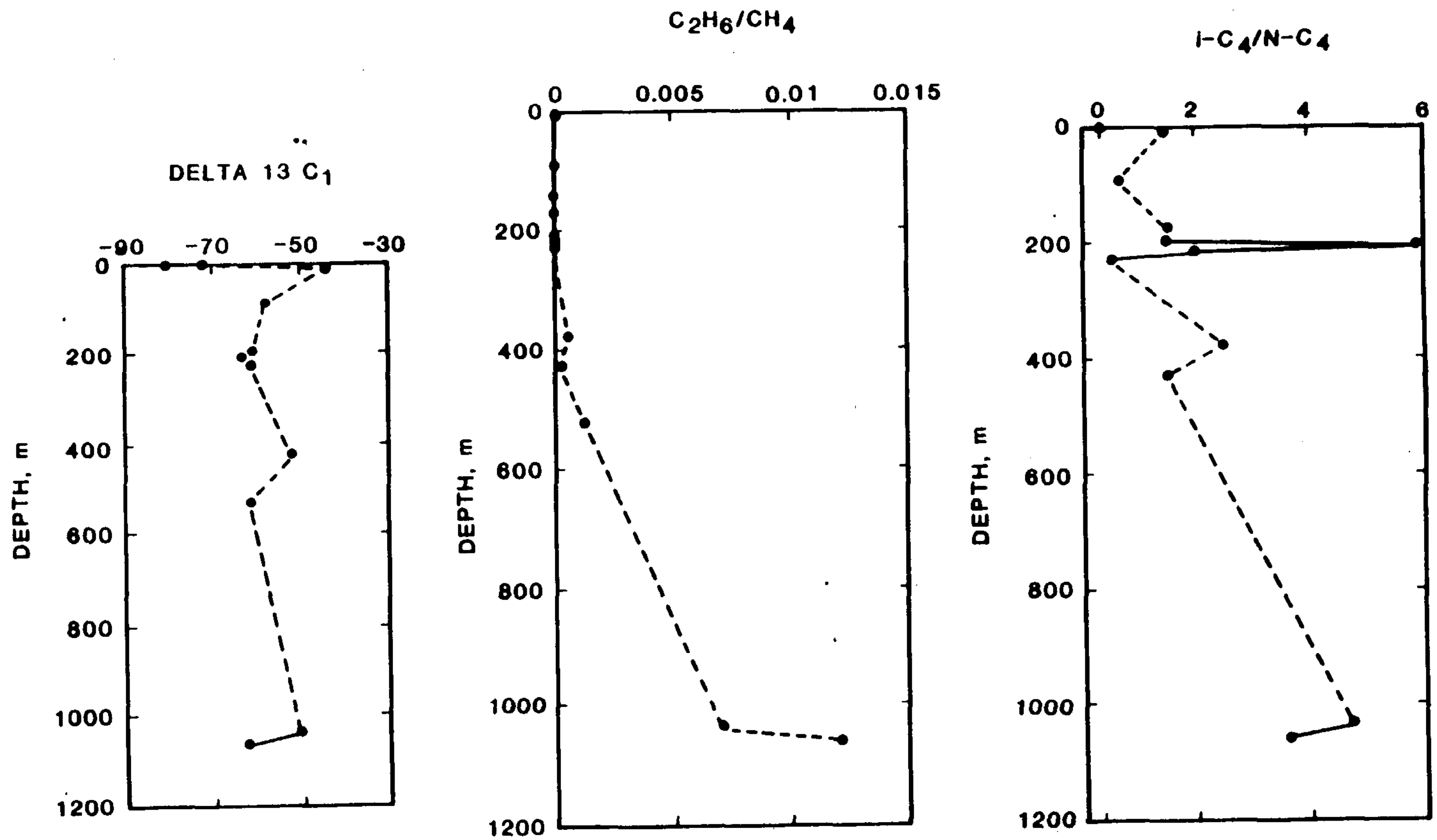


Figure 21. RESULTS OF ISOTOPIC AND CHEMICAL ANALYSES OF HYDROCARBON GASES AT DSDP SITE 380

After Faber et al., 1978

Thermogenic Hydrocarbons

The general lack of thermogenic hydrocarbons in sediments of the Black Sea to the subbottom depth 1,000 m has been ascertained by a number of authors (Kendrick et al., 1978; Hunt, 1974; Huc et al., 1978; McIver, 1978, and others). While the structural aspects of the Black Sea still remain obscure, the migration of thermogenically generated hydrocarbons cannot be ultimately precluded. In the meantime, despite an often satisfactory amount and type of organic matter in sediments, the analyses of kerogen as well as the temperatures encountered in the DSDP holes unequivocally indicate that the investigated sediments have not been buried deeply enough to reach the window of oil generation.

Heat Flow and Geothermal Gradient

The rate of natural heat flowing to the surface sediments of Earth is a net result of the amount of heat transmitted to the mantle, conductive properties of rocks, temperature at the surface, and often alternating tectonic events responsible for depositional or erosional processes. In the Black Sea region the latter group of factors is still not adequately known despite many attempts to explain the tectonic history of the region (Apolskiy, 1974; Adamiya et al, 1974; Brinkmann, 1974; Malinovskiy, 1967, and others). This fact has caused understandable difficulty in interpretation of the wide range of values of the heat flow obtained by various authors in the region of the Black Sea.

The measurements of heat flow in shallow sediments of the Black Sea were first reported by Sysoyeo (1963) and subsequently by Erickson (1970), Lubimova and Feldman (1970), Lubimova and Lavostin (1973), and Erickson and Simmons (1974). All these measurements, however, representing 78 heat flow values, did not yield a consistent picture of geothermal processes in the Black Sea basin. While the measurements were performed in shallow sediments, utilizing various methods, and the thermal conductivity ranged from 4 μcal/cm sec°C to 2 μcal/cm sec°C with occasional strong nonlinear thermal gradients, it is difficult to decide which ones represent reliable values. In this situation the thermal data obtained from the measurements at the DSDP sites seem to represent the most consistent and credible information to date.

A unique feature of the latter data is that they are based on probing deeper geological strata while a uniform methodology of measurements was applied over the whole investigated area. Apart from direct measurement of temperature of sediments at various depth intervals, the thermal conductivity measurements were made on sediment cores using the needle probe technique described by Von Herzen and Maxwell (1959). Also Ratcliffe's (1962) correction factors for downhole temperature and pressure were used in the final calculations of heat flow. Interested readers will find a detailed discussion of the methodology used in the paper by Erickson and Von Herzen (1978). Despite all precautions taken in order to assure the highest quality data, Erickson and Von Herzen (1978) conceded that the values of the conductivity may be systematically slightly low.

The temperatures and thermal conductivity values at Site 379 are shown in Table 11 and Figure 22. While the water depth at the location is 2,171 m,

TABLE 11.

DOWNHOLE TEMPERATURE DATA AND CALCULATED HEAT FLOW AT THE DSDP SITE 379, BLACK SEA, After Erickson and Von Herzen, 1978

Subbottom Depth m	Sediment Temperature °C	Thermal Gradient °C/100m	Thermal Conductivity mcal/cm sec°C	Interval Heat Flow (μcal/cm^2/sec)
0	9.00	4.40	2.38	1.05
35.0	10.54			
45.0	(12.57	3.21	2.41	0.77
94.5	12.45			
149.5	(<29.55)	3.33	2.70	0.90
198.2	15.90			
244.5	(<17.18)	3.42	2.85	0.97
292.0	(>18.72			
339.5	20.73	3.87	3.13	1.21
425.0	24.04)			
624.5	(27.69)			

sediment beneath is probably 10,000 m thick. The sedimentary strata to the depth of at least 1,000 m lie almost horizontally. The bottom water temperatures taken between the 23rd and 25th of May show variations within the 8.5 to 9.06°C interval. Five reliable temperature measurements of in situ sediments (Figure 22) yielded heat flow ranging from 0.77 to 1.21 μcal/cm^2 sec. The average value was 0.98 μcal/cm^2 sec with a standard deviation ±0.15 μ cal/cm^2 sec. The geothermal gradient is represented by a value of 3.42°C/100 m, which is relatively low for a marine area.

At DSDP Site 380, located at the foot of the continental slope in the southwestern part of the basin, the water depth is approximately 2,107 m. The reflectors on seismic lines from the area show smooth strata gently sloping up in a southwestern direction. Temperatures in the nearbottom water column measured in May were found to be about 8.4°C. Five temperature measurements of in situ sediment at subbottom depth between 104.5 and 370.5 appear to be reliable and fall on nearly straight line of geothermal gradient 3.5°C/100 m (Figure 23; Table 12).

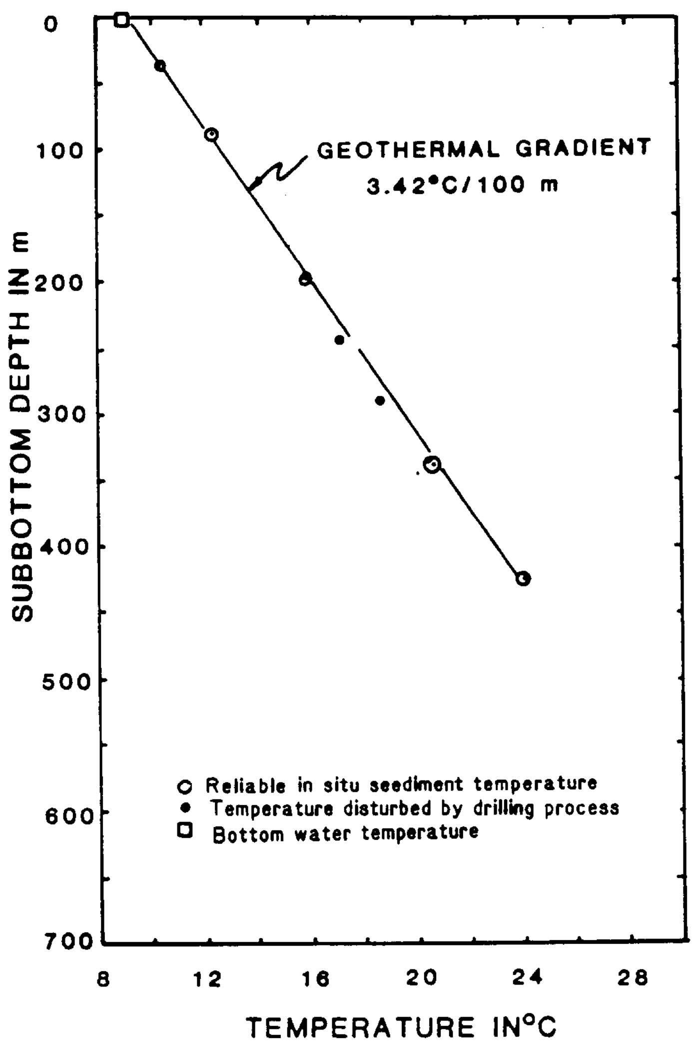


Figure 22. TEMPERATURE VERSUS DEPTH AT THE SITE 379

After Erickson and Von Herzen, 1978

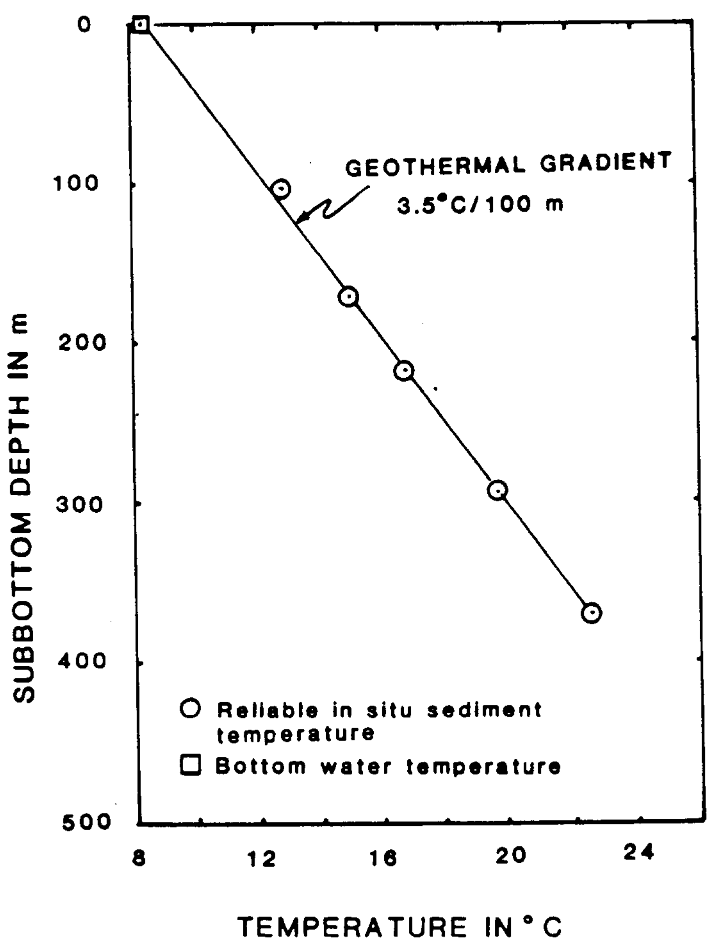


Figure 23. TEMPERATURE VERSUS DEPTH AT THE DSDP SITE 380

After Erickson and Von Herzen, 1978

TABLE 12.

DOWNHOLE TEMPERATURE DATA AND CALCULATED HEAT FLOW AT THE SITE 380, BLACK SEA, After Erickson and Von Herzen, 1978

Subbottom Depth m	Sediment Temperature °C	Thermal Gradient °C/100m	Thermal Conductivity mcal/cm sec°C	Interval Heat Flow (μcal/cm²/sec)
0	8.43			
86.5	(>11.24)	5.12	2.31	1.18
180.5	17.67	4.74	2.32	1.10
199.5	(<18.57)			
475.0	37.33			

The calculated heat flow on the basis of thermal measurements at DSDP Site 380 revealed average values and standard deviation of 0.99 ± 0.10 μ cal/cm^2 sec respectively. These values proved to be very close to those obtained from Site 379.

The results of thermal measurements in DSDP Hole 381 are shown in Figure 24 and Table 13.

TABLE 13.

DOWNHOLE TEMPERATURE DATA AND CALCULATED HEAT FLOW AT SITE 380, BLACK SEA, After Erickson and Von Herzen, 1978

Subbottom Depth m	Sediment Temperature °C	Thermal Gradient °C/100m	Thermal Conductivity mcal/cm sec°C	Interval Heat Flow (μcal/cm²/sec)
0	8.47	42.72	2.35	1.05
67.5	(>10.67)			
104.5	12.93			
142.5	(17.11)	31.4	2.54	0.80
171.0	15.02	39.6	2.57	1.02
218.5	16.90	37.9	2.70	1.02
294.5	19.78	38.9	2.72	1.06
370.5	22.74			
465.5	(25)			

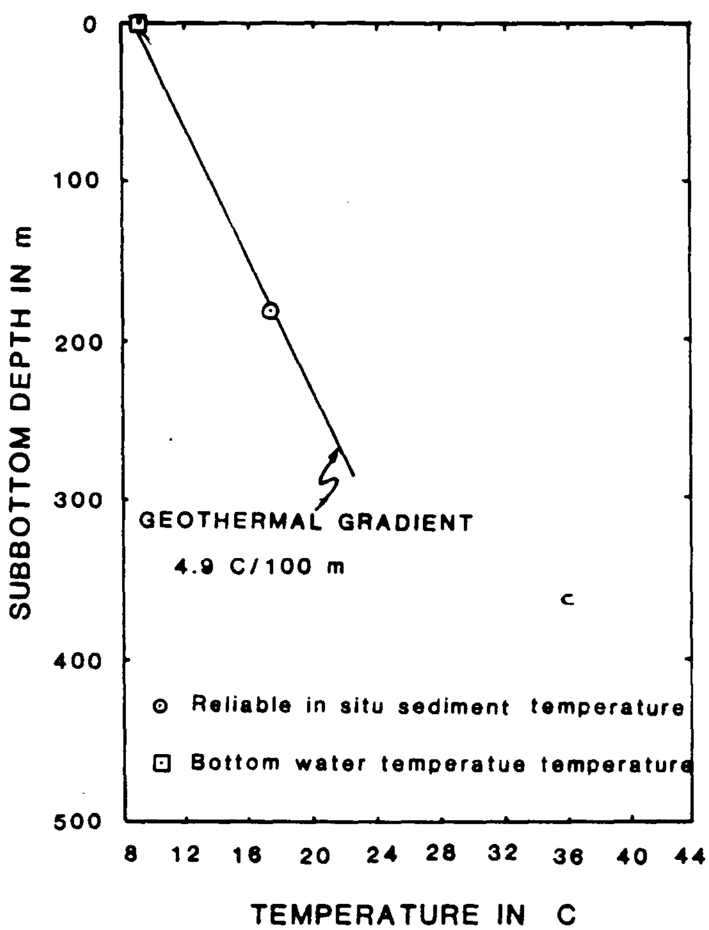


Figure 24. TEMPERATURE VERSUS DEPTH AT THE DSDP SITE 381

After Erickson and Von Herzen, 1978

The drilling site was located southwest of Site 380 where the total thickness of sedimentary strata is on a decreasing trend. The water depth at the location is approximately 1,722 m. Due to technical difficulties, the only reliable temperature data were obtained at a subbottom depth of 180.5 m. The calculated value of the heat flow is slightly higher compared with the previously described sites, showing the value 1.18 $\mu cal/cm^2$ sec. Also the geothermal gradient calculated on the basis of bottom water temperature and one reliable measurement of the in situ sediment temperature shows an increased value of 4.9°C/100 m.

In summary, it can be concluded that heat flow in the uppermost sediments of the Black Sea basin display relatively low values. The average heat flow value in the central part of the basin is 0.99 $\mu cal/cm^2$ sec, whereas slightly higher values have been observed in marginal parts of the basin. These values represent depressed heat flow due to the high rate of sedimentation in the Black Sea (Table 14).

The intensity of heat flow reduction due to high sedimentation rate is shown in Table 14, after Erickson and Von Herzen (1978). The latter authors made calculations pertaining to the heat flow decrease based on an assumption of the constancy of the rate of sedimentation over long periods of time.

The heat flow values can also be affected by changes of bottom water temperature by altering the thermal gradient ($\frac{dt}{dL}$). Deutser (1974) indicated that during the time 9,000 to 7,000 years ago, warmer Mediterranean waters were entering the Black Sea, thus warming up its waters. Although the thermal history of the Black Sea is still obscure, some authors have shown that annual fluctuations of water temperatures on sediment temperature follow an exponential function with depth (Jaeger, 1965; Pugh, 1975). Therefore, as the influence of water temperature changes may somehow affect shallow sediments, they are probably negligible with respect to deeper strata.

While the geothermal gradient is closely related to the heat flow, the thermal investigations at the Black Sea DSDP sites showed similar changes of the gradient within the basin. Presently the values of the geothermal gradient in the central part of the basin show relatively low values (3.5°C/100 m), with a tendency to higher values in the upper continental slopes and toward the margins of the basin.

Rate of Sedimentation

Based on seismic data, Neprochow et al. (1974) indicated that the total thickness of sedimentary sequences may exceed 15 km in the central part of the Black Sea. Adopting the assumption that the oldest sediments are of middle Cretaceous age (i.e. 100 million years), the average sedimentation rate is 60 to 120 m/million years. The calculated rates of sedimentation at DSDP Site 380 are presented in Table 13.

TABLE 14.

CORRECTED HEAT FLOW VALUES FOR THE SEDIMENTATION EFFECT IN BLACK SEA, After Erickson and Von Herzen, 1978

Site	Sediment Thickness (km)		Thermal Diffusivity (cm^2/sec)	Observed Heat Flow (10^{-6} cal/cm^2sec)	Heat Flow (10^{-6} cal/cm^2sec) Corrected for Sedimentation for Length of Time Shown Below					
	Observed	Expanded			20 m.y.	40 m.y.	60 m.y.	80 m.y.	100 m.y.	200 m.y.
379	8	24	0.008	0.98	3.82	2.48	2.07	1.86	1.73	1.46
380	5	15	0.006	0.99	2.55	1.90	1.68	1.56	1.48	1.31
381	3	8	0.004	1.18	2.14	1.79	1.65	1.57	1.53	1.42

TABLE 15.

SEDIMENTATION RATES AT THE DSDP SITE 380, After Asu, 1978

Depth m	Age Stage or Epoch	m.y.	Nature of Sediments in Interval	Average Rate of Sedimentation, m/m.y.
76	Eemian Interglacial	0.125	Terrigenous, mainly glacial	600
328	Near Top A	0.63	Terrigenous, glacial and interglacial	500
680	Base Alpha	1.75	Terrigenous and chemical, mainly glacial some interglacial	310
868	Base Pliocene	5.2	Terrigenous and chemical preglacial	54
972	Messinian	6	Coarse terrigenous and chemical, preglacial	103
1075	Late Miocene	8 or 10	Black shale	51 or 26

The rate of sediment deposition in the Black Sea during the late Quaternary is about 100 m/million years. Very high sedimentation rates (300 to 600 m/million years) continued throughout the Pleistocene, particularly during periods of glaciation. These rapidly deposited sediments were found to subbottom depths of approximately 700 m at Site 380. During the periods with dominant chemical sedimentation, the deposition rates dropped significantly. Increased values of sedimentation during the Messinian stage is mainly due to coarse clastic deposition during subaerial exposure of the surrounding areas. The deposition of black shales is probably a product of the marine-brackish sedimentation where lack of coarse terrigenous material and chemical precipitation was marked by a relatively low (26 m/million years) rate of sedimentation.

The highest rate of depositional processes (1,080 m/m.y., based on uncompacted thickness of sediments) was found at DSDP Site 379, whereas the lowest average value (163 m/m.y.) was revealed at Site 381.

A composite picture of the sedimentation rates within the Black Sea region is shown in Figure 25.

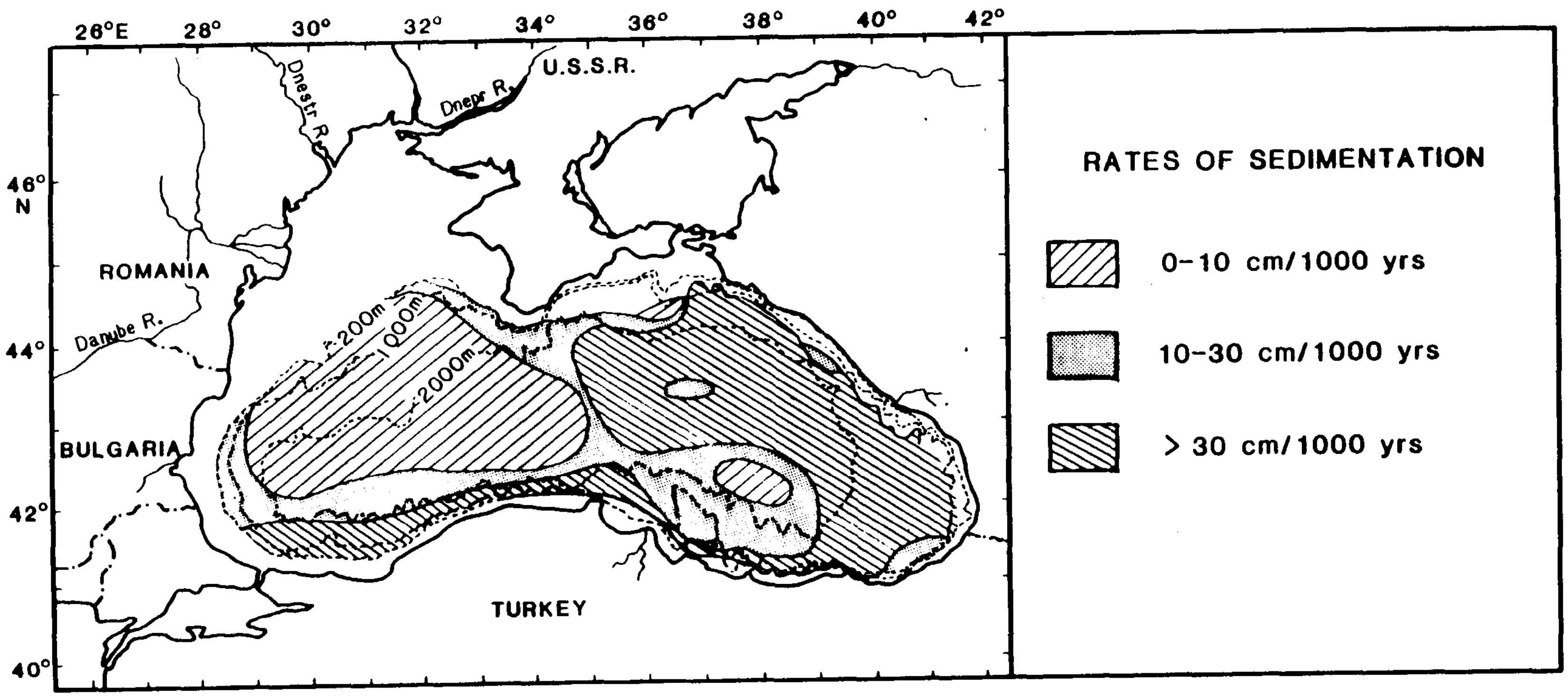


Figure 25. **SEDIMENTATION RATES IN THE BLACK SEA DURING THE PAST 3000 YEARS**

After Ross et al., 1970

PART II

FORMATION AND STABILITY OF GAS HYDRATES

The Black Sea represents an unusual geological environment with respect to the major conditions necessary for gas hydrate formation. Perhaps the single most important feature of the basin is widespread active biogenic methanogenesis directly related to the presence of chemically reducing conditions from the sea depth of 100 to 150 m. The presence of relatively high concentrations of dissolved methane as well as methane in free state in pore water in conjunction with a favorable range of temperature and pressure, should result in gas hydrate occurrence in at least some areas of the Black Sea region. Yet, even though a number of cores were recovered from various sections of the region, and despite common reports about vigorous bubbling gas from these cores, gas hydrate has been confirmed at only one location. Yefremova and Zhizhchenko (1972) reported cores containing frost-like gas hydrate crystals recovered by the Soviet crew at the unspecified location of "the station 116". It was also stated that sea water depth at station 116 is 1,950 m and the above mentioned gas hydrates were found at 6.40 to 8.10 m subbottom depth. Vague information on gas hydrate occurrence in the Black Sea was published by Makogon (1974) who wrote:

> Some of the Black and Caspian Sea cores bubbled with gas from top to bottom. On breaking open freshly-extracted cores, frost-like hydrate crystals could be observed inside the pore spaces.

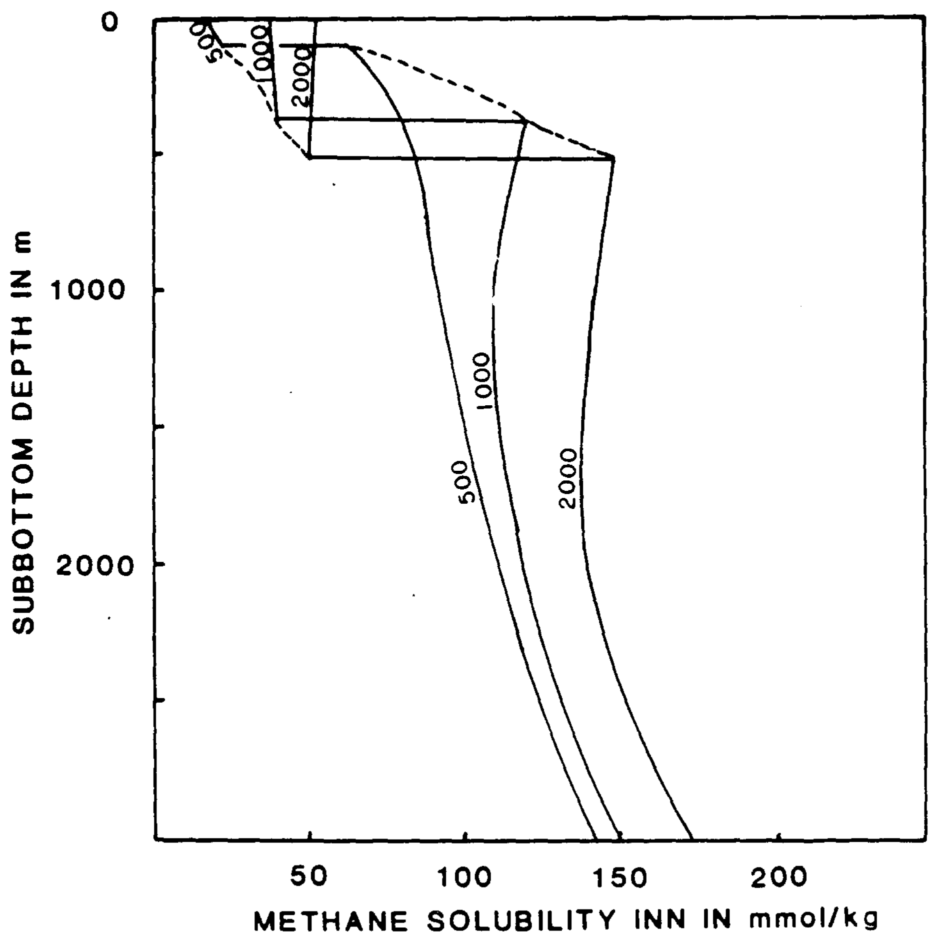
Considering the fact that none of these cores from the Black Sea was recovered using pressure core barrel (PCB), it is highly probable that reported gases escaping from the recovered cores and cavities in the sediment (McIver, 1978; Hunt et al., 1978) are in some instances partially the remnants of dissociated gas hydrates. The definite explanation of these gas occurrences will require the usage of PCB type coring devices capable of preventing gas hydrate dissociation in the process of core recovery.

Pore Water Saturation in Methane

The availability of hydrocarbon gases together with proper temperature and pressure is a principle condition for gas hydrate formation. Numerous investigations in the Black Sea revealed significant amounts of gas escaping from cores upon their recovery. Based on the observation data from the Atlantis II cruise, McIver (1978) noted that gas in freshly recovered cores "caused substantial expansion of the sediment and formation of gas gaps up to 15 cm long along the length of some cores." Also Hunt et al. (1978) reported that "gases from the cores brought to the surface caused the core sections to be separated, and some cores contained sufficient gas to blow the core out the end of the barrel." These observations, although valuable, are largely qualitative in their nature.

The optimal gas:water ratios under which gas hydrate formation occurs in the most efficient way are not adequately known. A number of lab experiments proved, however, that relatively high gas concentrations in the presence of water molecules is indispensable (Makogon, 1974; de Boer et al., 1985). For example, in their experiment, de Boer et al. (1985) used a 70 cm long tube with an internal diameter of 2.5 cm, filled with coarse, well sorted sand. The permeability of such material was 200mD. While propane gas was used at a flow rate of 0.5 ml per hour, the injection of only a few cubic centimeters of water caused the sharp decrease of permeability to almost zero in 15 minutes due to gas hydrate formation. In natural geological environments, such favorable conditions may exist in the transition zone between water and gas zones in structural hydrocarbon traps. The Messoiakh field is a prime example of such favorable conditions for gas hydrate formation. Another conceivable mechanism leading to gas hydrate generation in natural environments is change in gas solubility in water. Claypool and Kaplan (1974) have shown the relationship between the equilibrium solubility of methane in water and gas hydrate stability (Figure 26). The chart in Figure 26 was constructed for 2°C bottom water temperature, geothermal gradient of 3.5°C/100 m, and hydrostatic pressure gradient 10.1 kPa/m, on the basis of experimental data of Culberson and McKetta (1951) on CH_4 solubility in water. The curves in the diagram show slight CH_4 solubility changes with depth. For water columns 500 to 4,000 m thick, the solubilities range from 25 mmol to 60 mmol per 1 kg of pore water. The abrupt change of CH_4 solubility for each water column category coincides with the lower boundary of gas hydrate stability. If the CH_4 saturation at given P-T conditions exceeds the limit of solubility, the methane hydrate is stable in this zone.

In view of the above presented data, it is obvious that proper assessment of gas hydrate formation and stability must be based on in situ gas concentration in water. Only limited Russian data on gas content in nearbottom sediments from the western Black Sea are presently available (Table 16). According to Ivanov et al. (1984), these data were obtained using hermetic vacuum core liners which enabled the measurement of in situ volume of gas per sediment unit. In order to bring these data to commonly used units, mmol per 1 kg of pore water, the overcalculated values are shown in Table 16.



(numbers on curves indicate sea depth in meters)

Figure 26. RELATIONSHIP BETWEEN METHANE SOLUBILITY AND GAS HYDRATE FORMATION

After Claypool and Kaplan, 1974

TABLE 16.

METHANE CONCENTRATIONS IN SEDIMENT AT SOME STATIONS OF BLACK SEA, After Ivanov et al., 1984

Station	Sea Depth m	Subbottom Depth cm	Methane Concentration mmol/kg of pore water
577	106	30-40	0.094
578	91	30-40	0.023
580	193	20-30	0.005
		110-120	0.011
		210-220	1.89
581	860	40-50	0.023
		180-290	0.16
		140-160	0.12
		200-210	0.708
584	220	200-220	0.13
590	59	30-40	0.019
		90-100	1.44
		100-120	2.8
		100-110	0.44
		190-200	1.56
		300-310	0.76
601	1065	30-40	0.0013
		140-160	0.89
		250-260	2.049
		380-390	0.036
602	800	20-30	0.014
603	233	20-30	0.01
		100-110	1.606
		200-210	1.24
		300-310	0.33
543	1750	55-60	0.01
		320-330	0.49
544	2108	100-110	0.01
		250-260	0.01
		310-320	0.03
551	80	180-200	0.01
571	1450	70-80	0.11
		180-200	0.38
		300-320	0.54
576	850	200-210	0.83
		300-340	0.94

Several important conclusions can be drawn from this listing:

1. The greatest concentrations of CH_4 in nearbottom sediments occur at a depth of 0.1 to 0.3 m.

2. Horizontal distribution of CH_4 in nearbottom sediments show significant variations which most likely reflect various contents of the organic matter available for methanogenesis.

3. Methane concentrations in the sediments ranging from .01 mmol to 2.05 mmol per 1 kg of pore water represent largely undersaturated water within 3 m of nearbottom sediments.

4. With respect to CH_4 concentrations, the zone of nearbottom sediment features mostly unfavorable conditions for gas hydrates.

Gas Hydrate Equilibrium Conditions

Once the gas-water interface is present, the equilibrium of gas hydrate formation is mostly controlled by temperature and pressure. Further stability of the gas hydrate is defined by vapor pressure of hydrate and water (Barkan and Voronov, 1982). The numerous experimental data have shown that marginal P-T conditions of gas hydrate formation in geological environments may vary. The variations are mainly due to such factors as: porosity, type of sediment, type of available gas, and salinity of pore water. The modifying role of these factors has been discussed in some of our previous reports of this series (Krason and Ciesnik, 1985; 1986). Therefore, only the general role of these factors will be highlighted here. Russian lab experiments revealed that lower temperatures and higher pressures are needed for gas hydrates to form, compared with free gas-water interface (Makogon, 1974). With lower porosity, the depression of water vapor pressure is greater. Thus, lower temperature is required for initiation of hydrate formation with decreasing porosity. The type of sediment has bearing on heat flow, as various rocks represent differences in heat conductivity. Typically, increased thermal conductivity can be observed in strata with higher sand:shale ratio, which means that lower geothermal gradients can be anticipated. Carbonate sequences have higher thermal conductivity than sands (MacLeod, 1982). With reference to the type of gas, it has been established that distinction must be drawn between methane gas and multicomponent hydrocarbon gases. The admixture of higher homologues shifts the temperature necessary for gas hydrate stability toward higher values and lower pressures. Conversely, increased salinity of water requires lower temperatures and higher pressures for gas hydrate formation and stabilization.

In the Black Sea, where geothermal gradients are known from direct measurements at DSDP Sites 379, 380 and 381, methane appears to be a prevailing gas in sediments, and pore water does not display drastic changes. Therefore, only changes in porosity could contribute to slightly altered values of temperature and pressure necessary for gas hydrate stability. The maximum depths of the hydrate zone in the Black Sea at various sea depths, and geothermal gradient changing from 3.5°C/100 m to 4°C/100 m, are shown in Figure 27. The chart is based on the experimental data obtained by John (1981) for biogenic methane at the free gas-water interface. Therefore, the real lower boundary of the hydrate zone should be moved slightly upward.

On the basis of these data, the minimum sea depth at which gas hydrates may form when a sufficient amount of methane is available is approximately 900 m. At a 2000-m sea depth, the lower boundary of the gas hydrate zone appears to be at 322 m below the sea bottom.

Seismic Data

Seismic data are frequently used as indirect evidence of gas hydrate presence in marine environments. Anomalous seismic reflectors often referred to as bottom simulating reflectors (BSRs), often seen on the marine seismic records, have been interpreted by many authors as the base of gas hydrate zones (Ewing and Hollister, 1972; Dillon et al., 1980; and others). Besides compliance with temperature and pressure stability conditions of gas hydrates, Bryan (1974) and Shipley et al. (1979) suggested considering three features of BSRs in identifying their relationship with gas hydrate zones. These features are:

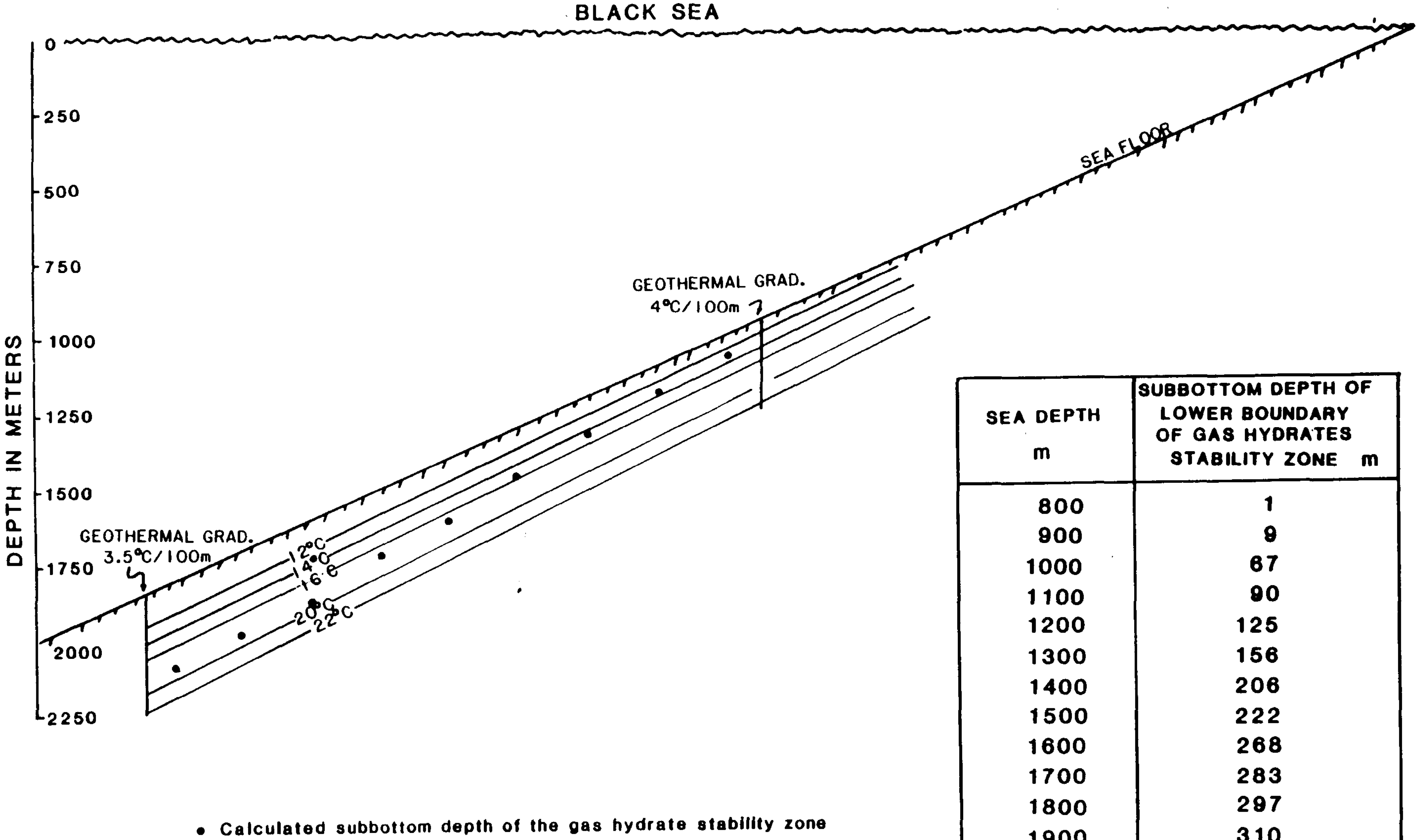
1. reflection polarity reversal
2. large reflection coefficient
3. increased subbottom depth of the BSR with increasing water depth.

The concentration of free gas below the gas hydrate zone should alter the formation density and acoustic velocities. Therefore, the boundary between the gas hydrate zone and free gas zone should be reflected by the seismic polarity reversal and negative reflection coefficient.

Review of approximately 4,300 miles of seismic lines from the Black Sea collected by the Woods Hole Oceanographic Institute did not reveal apparent reflectors which could be interpreted as gas hydrate related seismic responses. Although abundant gas hydrate horizons are not likely to occur in the region, identification of the BSR is extremely difficult due to the lack of deformed sediments in most of the region. Since the stratification of the sediments is mostly parallel to the sea floor (Figure 28), gas hydrate-related bottom simulating reflectors (BSRs) could at best be identified as enhanced reflectors parallel to the general stratification lines.

Assessment of Gas Resources in Gas Hydrates

The presence of gas hydrates in the Black Sea has been confirmed at station 116 (Yefremova and Zhizhchenko, 1972; Makogon, 1974). Despite some characteristics of the area published by Russians, we were unable to identify the exact location of the station. Russians also noted the presence of ice-like frost in freshly broken cores in some unspecified locations in the



SEA DEPTH m	SUBBOTTOM DEPTH OF LOWER BOUNDARY OF GAS HYDRATES STABILITY ZONE m
800	1
900	9
1000	67
1100	90
1200	125
1300	156
1400	206
1500	222
1600	268
1700	283
1800	297
1900	310
2000	322
2100	333

Calculations of the maximum depth of the gas hydrate zone are based on the experimental data by Holder (in Handbook of Gas Hydrate Properties and Occurrence, 1983)

Figure 27. GAS HYDRATE STABILITY ZONE IN THE BLACK SEA

Figure 28, Seismic line across southwestern part of the Black Sea, is located in the pocket at the end of the report.

Black Sea. Yet, lack of gas hydrate occurrence in a large number of shallow nearbottom cores recovered from the Black Sea does not seem to be unexpected. Although the region is characterized by relatively high biomethanogenesis, the analyses of recovered sediments from at least the western part of the region show a degree of gas concentration in water generally insufficient for gas hydrate formation. It appears that in the area of the Black Sea where sea depth exceeds 900 m, the potential gas hydrate accumulations are controlled by the availability of sufficient amounts of methane. The areas fulfilling such conditions probably have a patchy distribution throughout the region. Conceivably these areas are represented by pockets of sediments with increased porosity and permeability.

The total area with P-T conditions favorable for gas hydrate stability in the Black Sea amounts to 251,166 km^2. Assuming 40% sediment porosity and 10% pore space filling, 4% of the sediment would be filled with gas hydrates. Applying the 200:1 gas volume conversion factor from gas hydrates (Kuuskraa, 1983) for standard conditions and 1% areal extent of hydrates, the estimated gas reserves in hydrate state should be as follows:

1 m thickness x 2.5 x 10^{11} m^2 area x 4% hydrate x 1% aerial extent x 200 volume conversion factor = 2 x 10^{10} m^3 (0.7 TCF)

1 m=2 x 10^{10} m^3 (0.7 TCF)
100 m=2 x 10^{12} m^3 (70 TCF)
200 m=4 x 10^{12} m^3 (140 TCF)
300 m=6 x 10^{12} m^3 (210 TCF)

Conclusions

The Black Sea, which extends for over 432,000 km^2, is the world's largest enclosed marine basin. This feature, in conjunction with continued subsidence since early Tertiary, has primarily defined the history of sedimentation. The region is still in the early stage of exploration where many questions in the fields of structural geology, sedimentology, and geochemistry remain unanswered. Analysis of principal geological factors necessary for gas hydrates to occur made it possible to draw the following conclusions:

1. The seismically derived thickness of the sedimentary sequence reaches 16,000 m in the central part of the Black Sea basin, and decreases quite rapidly toward its margins.

2. The entire basin has been subsiding continuously since at least early Tertiary.

3. The oldest sediments of upper Miocene age were encountered at the DSDP Site 380 (1,075 m of subbottom depth).

4. The late Tertiary-Quaternary sediments in the Black Sea basin revealed three sedimentological stages:

   a. black shale sedimentation
   b. periodic chemical deposition
   c. terrigenous sedimentation

   These changes of sedimentation type most likely reflect changes of the sea level as well as climatic fluctuations.

5. Rates of sedimentation in the basin appear to be high, ranging from 50 to 600 m/m.y.

6. Undisrupted sedimentation of the upper sequences of the sediment column resulted in lack of major deformations of the strata.

7. Heat flow, calculated on the basis of thermal measurements at the DSDP sites, has shown relatively low values, producing geothermal gradients from 3.5°C/100 m to 4.4°C/100 m.

8. Although with regard to temperature and pressure conditions over 255,000 km^2 could be considered as favorable for gas hydrate formation, the hydrocarbon gases availability diminishes this area severely.

9. Hydrocarbon gases in sediments of the Black Sea proved to be almost entirely of biogenic origin.

10. Despite the presence of an extremely favorable environment for biomethanogenesis, the methane content in sediments is usually well below the saturation level, i.e. outside the gas hydrate stablity area.

11. There are probably locations with favorable P-T conditions for gas hydrates where higher accumulations of methane enabled formation of the gas hydrates.

12. Assuming that such locations may occur in 1% of the previously mentioned 255,000 km^2 area, the assessed gas resources for 1 m thick hydrate zone amount to 2×10^{10} m^3 (0.7 TCF).

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